**US Army Corps
of Engineers**
Waterways Experiment
Station

Removal of RDX, TNB, TNT, and HMX from Cornhusker Army Ammunition Plant Waters Using Adsorption Technologies

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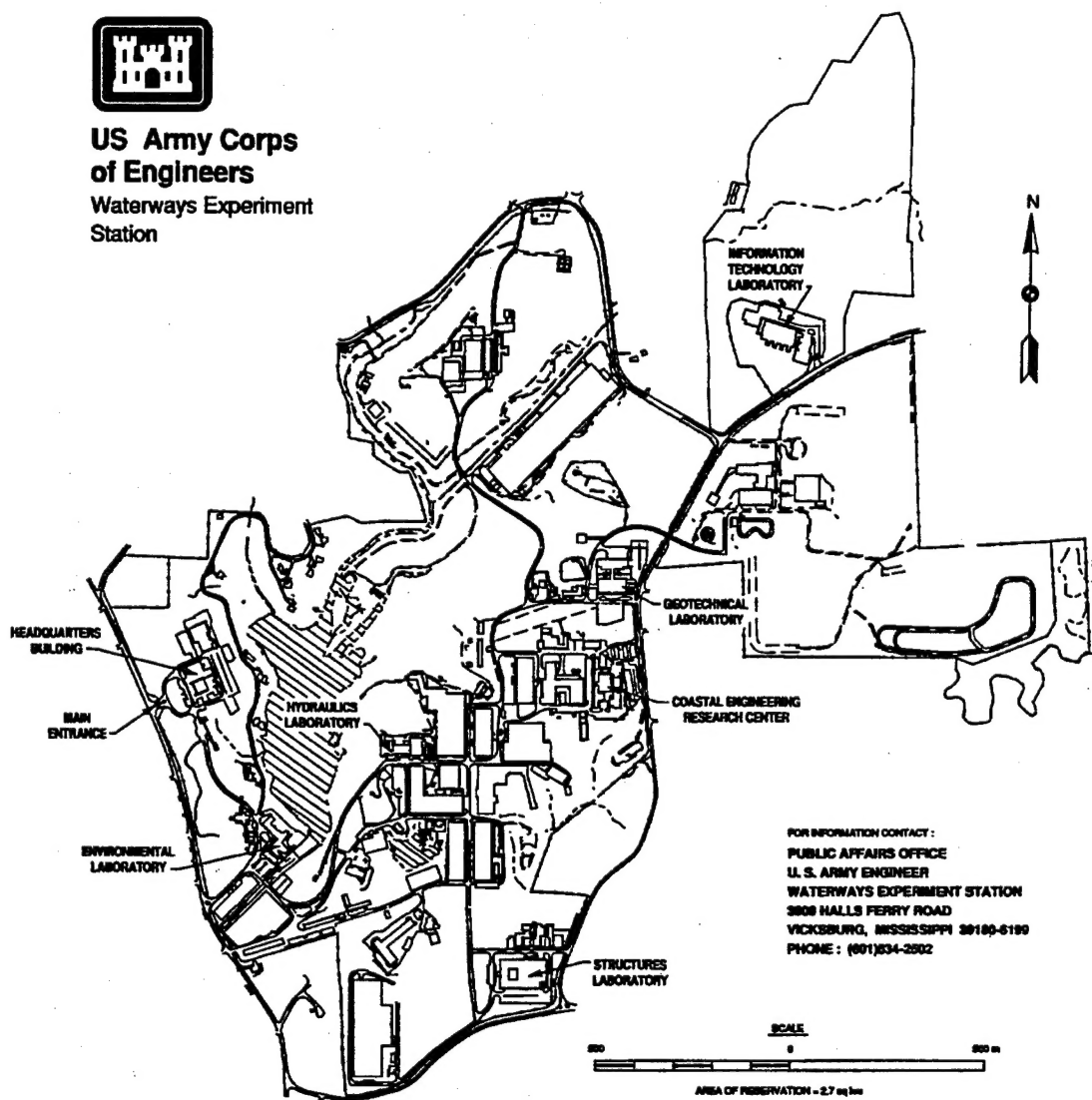Omaha, NE   68102-4978

Final report

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STRUCTURES
LABORATORY

SCALE

AREA OF RESERVATION = 2.7 sq km

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Preface

The work reported herein was conducted by the U.S. Army Engineer Waterways Experiment Station (WES) for the U.S. Army Environmental Center and the U.S. Army Engineer District, Omaha.

This report was prepared by Ms. Elizabeth C. Fleming, Environmental Restoration Branch, Environmental Engineering Division (EED), Environmental Laboratory (EL), WES; Mr. Randy Cerar, U.S. Army Environmental Center; and Mr. Ken Christenson, U.S. Army Engineer District, Omaha.

This work was conducted under the supervision of Mr. Norman R. Francingues, Chief, EED, and Dr. John W. Keeley, Director, EL.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander was COL Bruce K. Howard, EN.

This report should be cited as follows:

1 Introduction

Background

The Cornhusker Army Ammunition Plant (CAAP) is located in Grand Island, NE, and occupies 11,936 acres (4,832.32 ha) in Hall County. Figure 1 illustrates the general location of the CAAP, approximately 147 miles (236.57 km) east of Omaha, NE. The installation was constructed in 1942 to support World War II efforts and employed approximately 4,000 personnel. The CAAP is classified as a load, assembly, and pack facility and was used during the war for manufacturing bombs. On 1 September 1945, the CAAP was declared surplus, and the War Assets Administration had set in motion a disposal program for getting rid of equipment and materials. In 1946, the status was changed to standby; in 1950, the CAAP became a Government-owned contractor plant and was operated by Mason and Hanger - Silas Mason Company, Inc. On 1 December 1951, the plant was reactivated, but in 1956 the CAAP was placed on standby and remained that way until 1965. On 13 September 1965, the CAAP was reactivated with Mason and Hanger again operating the plant. On 12 October 1973, CAAP was again declared inactive, and total standby status was in effect by 1 July 1974. In 1989, the installation was declared excess by U.S. Army Armament Munitions and Chemical Command (AMCCOM) and remains in that status to date. Currently, the CAAP employs approximately three personnel. The CAAP's primary mission is the maintenance and protection of its inactive facilities so that if necessary, rehabilitation and resumption of manufacturing activities could be initiated.

In 1981 and 1982, the U.S. Army Environmental Center (USAEC) identified cyclotrimethylenetrinitramine (RDX), trinitrotoluene (TNT), and dinitrotoluene (DNT) contamination on-post. In 1983 and 1984, off-post studies indicated that contaminants had migrated up to 3 miles (4.828 km) off-post and had affected the drinking water of approximately 350 residents. In January 1984, the U.S. Army began providing bottled water to those residents whose wells were affected by explosives contamination. In August 1984, the Army made arrangements for the city of Grand Island to supply water to those residents whose wells were affected; by October 1985, the residents were receiving water through the city water supply system.
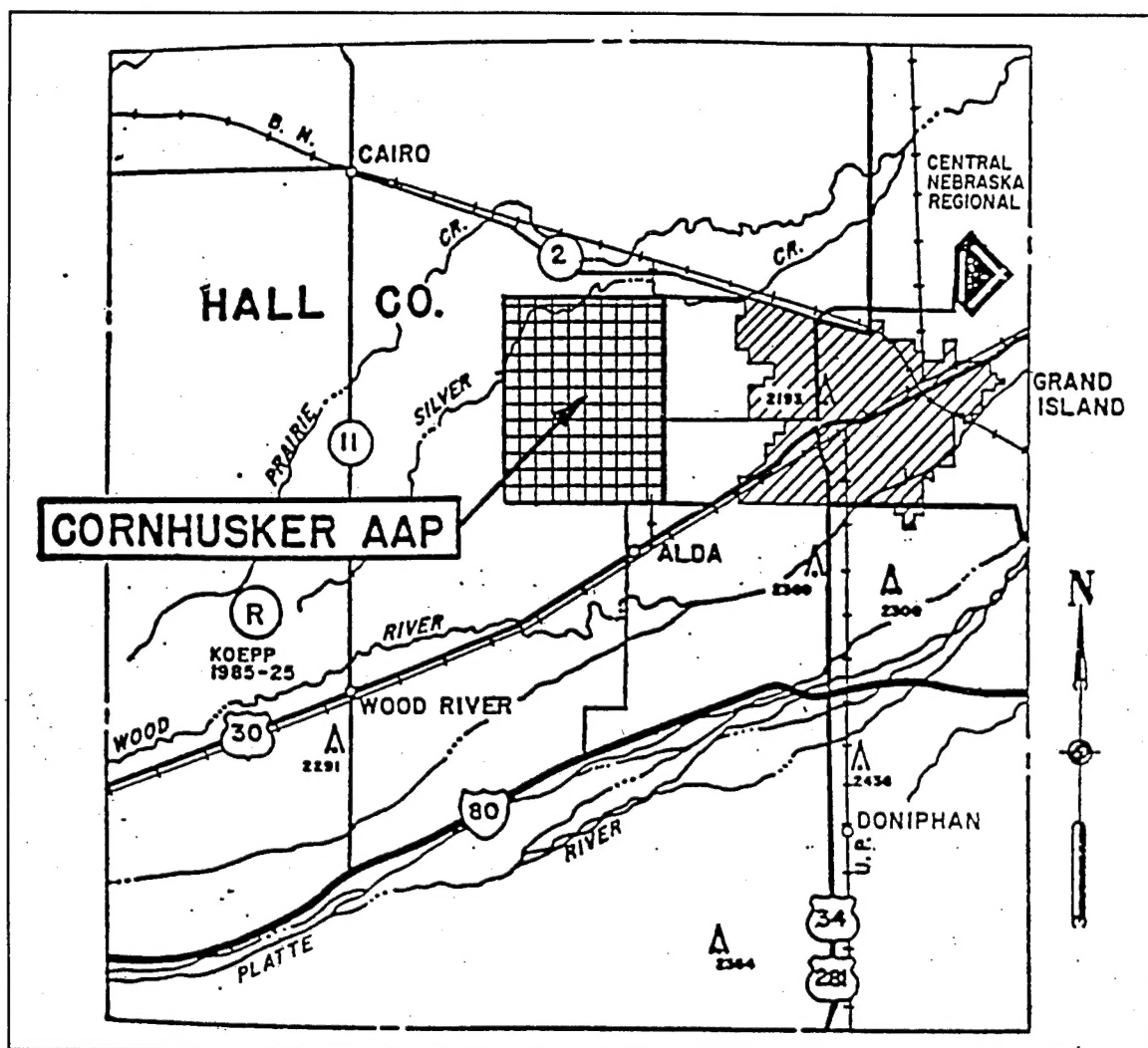
Figure 1.   General map of CAAP

The USAEC has been responsible for coordination of soils cleanup activities, which include incineration of explosives-contaminated soils from the source areas. The soils cleanup is part of the Installation Restoration Incineration Program, and excavation and incineration of the explosives-contaminated soils have been completed.

The USAEC and the U.S. Army Engineer District, Omaha, requested that the U.S. Army Engineer Waterways Experiment Station (WES) perform a bench-scale evaluation of adsorption technologies and ultraviolet/chemical oxidation (UVChO) for groundwater cleanup. The proposed groundwater treatment system will be designed to capture the explosives-contaminated groundwater plume. In efforts to hinder further migration and remediate the plume, the system will be treating groundwater extracted from wells at both the source (on-post) and distal (off-post) ends of the plume. This report addresses the adsorption portion of the study. Bench-scale tests were

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conducted in the WES Hazardous Waste Research Center (HWRC), and analyses were performed by the WES Environmental Chemistry Branch (ECB).

Treatment Requirements

The U.S. Environmental Protection Agency (USEPA) health advisory levels for RDX, trinitrobenzene (TNB), and TNT are 2 $\mu g/\ell$ and for cyclotetramethylenetetranitramine (HMX), 400 $\mu g/\ell$. HMX concentrations in the CAAP waters are approximately 33.9 $\mu g/\ell$, well below its drinking water standard. RDX, TNB, and TNT concentrations are approximately 33.5, 110.8, and 246.1 $\mu g/\ell$, respectively, exceeding the drinking water standards.

Project Objective

The main objective of this study was to determine the efficiency of several traditional and innovative adsorption processes for removal of RDX, TNB, TNT, and HMX from CAAP waters. Specific objectives of the adsorption studies are listed below.

a. To reduce RDX, TNB, TNT, and HMX to the target levels. The target levels for this study were the drinking water standards of 2 $\mu g/\ell$ for RDX, TNB, and TNT. HMX concentrations in the CAAP waters were below the drinking water standard.

b. To identify the most effective adsorbents for removal of RDX, TNB, TNT, and HMX.

c. To determine the adsorption capacity of the three most effective adsorbents for removal of RDX, TNB, TNT, and HMX.

d. To determine whether the adsorbents could be regenerated and subsequently reused for further treatment of CAAP waters.

Project Approach

The project was conducted in three phases: preliminary tests, isotherm studies, and regeneration studies. All three phases were conducted in the WES HWRC. Figure 2 presents a schematic diagram of the technical approach to the study conducted by the WES Environmental Restoration Branch. Preliminary tests were conducted to determine the optimal adsorbents to be further evaluated in isotherm studies. The three most effective adsorbents were evaluated in isotherm studies to determine the adsorption capacity (milligrams/gram) of each adsorbent for RDX, TNB, TNT, and HMX. The
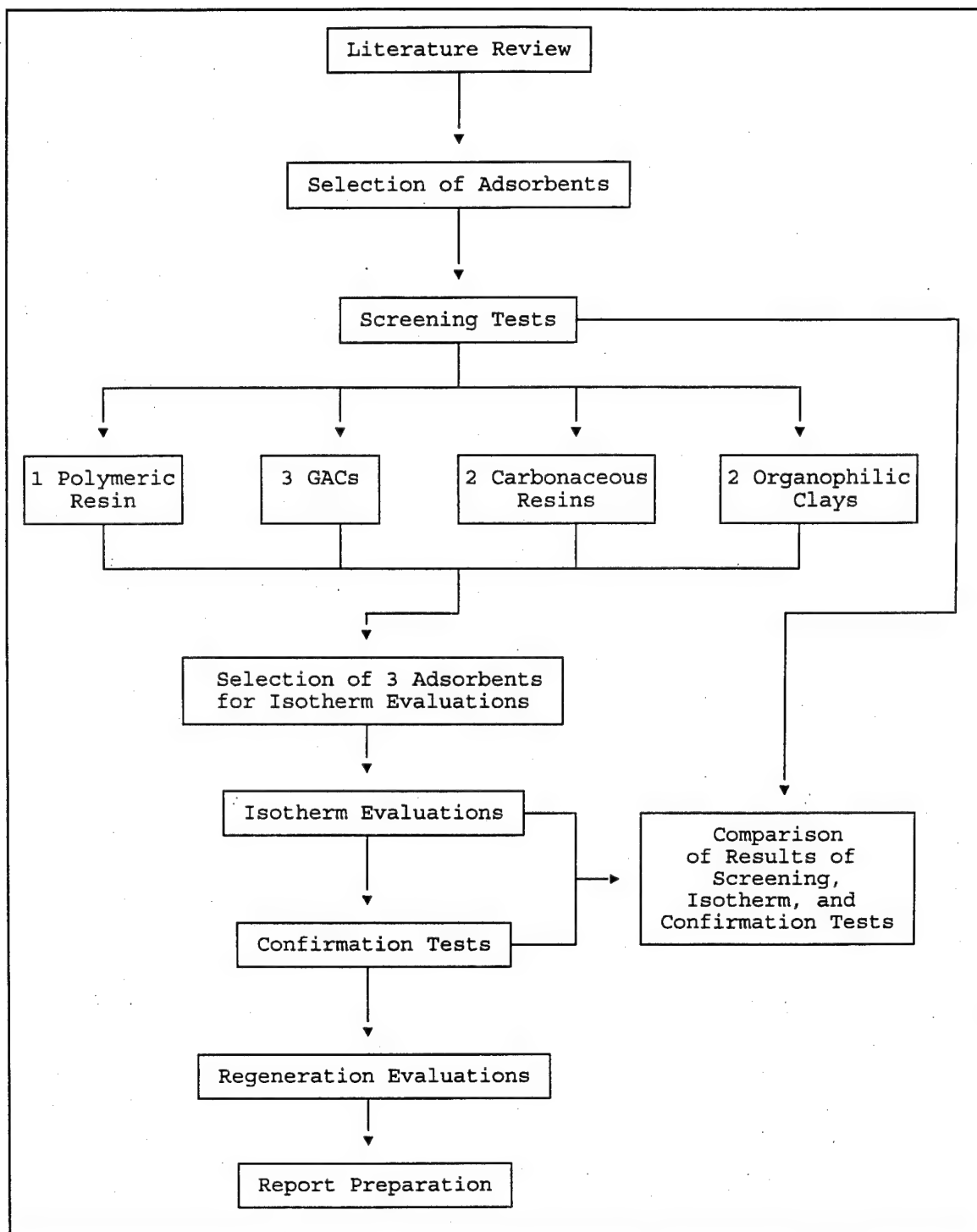
Figure 2. Schematic diagram of technical approach to study

three most effective adsorbents were evaluated in regeneration studies. More specifically, the study involved the following:

a. Literature review of vendor product information and historical data for removal of RDX, TNB, TNT, and HMX using adsorbents.

b. Selection of adsorbents for the preliminary tests.

c. Preliminary tests of six granular-activated carbons (GACs), two carbonaceous resins, one polymeric resin, and two organophilic clays followed by selection of adsorbents for isotherm evaluations.

d. Isotherm evaluation of the three optimal adsorbents for removal of RDX, TNB, TNT, and HMX.

e. Confirmation of the results of the isotherm evaluations.

f. Evaluation of the three optimal adsorbents in regeneration studies.

2 Technology Description

Physisorption/Chemisorption

Adsorption can occur at solid-solid, gas-solid, gas-liquid, liquid-liquid, or liquid-solid interfaces. Carbon treatment of water involves interactions at the liquid-solid interface. Adsorption is caused by attractive forces associated with either physisorption or chemisorption or a combination of the two (Cheremisinoff and Ellerbusch 1978). Both forces occur when molecules from the liquid phase become attached to the solid phase, overcoming the kinetic energy of the adsorbate molecules.

Physisorption is the result of weak intermolecular forces known as van der Waals' forces and is reversible. Van der Waals' forces consist of attraction-repulsion interactions that total to give the potential energy of the system (Faust, Aly, and Osman 1987). Physical adsorption does not involve the sharing or transfer of electrons and thus always maintains the individuality of interacting species. Physisorption processes are multilayered with more layers of adsorbate molecules forming on the adsorbent at higher concentrations. Physisorption is the most common type of adsorption. Chemisorption results in a chemical change of the adsorbate and is irreversible. Chemisorption processes are monolayered and require energy input to remove the adsorbate.

For liquid-solid systems, adsorption is the result of either or both of two processes, a lack of affinity of the adsorbate for the solvent or an affinity of the adsorbate for the adsorbent. Adsorption occurs in three basic steps. The first step is transfer of the adsorbate to the surface of the adsorbent. The second step is diffusion of the adsorbate from the adsorbent surface to the adsorption site within the adsorbent particle. The third step is adsorption of the solute on the interior surfaces, filling up the pore and capillary spaces of the adsorbent. A diagram of the pores within a carbon particle is illustrated in Figure 3 (Bricka and Fleming 1995).

Most solutes contain more than one adsorbate, so the preference for adsorption strongly affects the process removal efficiency. The presence of multiple adsorbates also affects the overall effluent quality and thus the ability of the process to meet the effluent quality criteria.
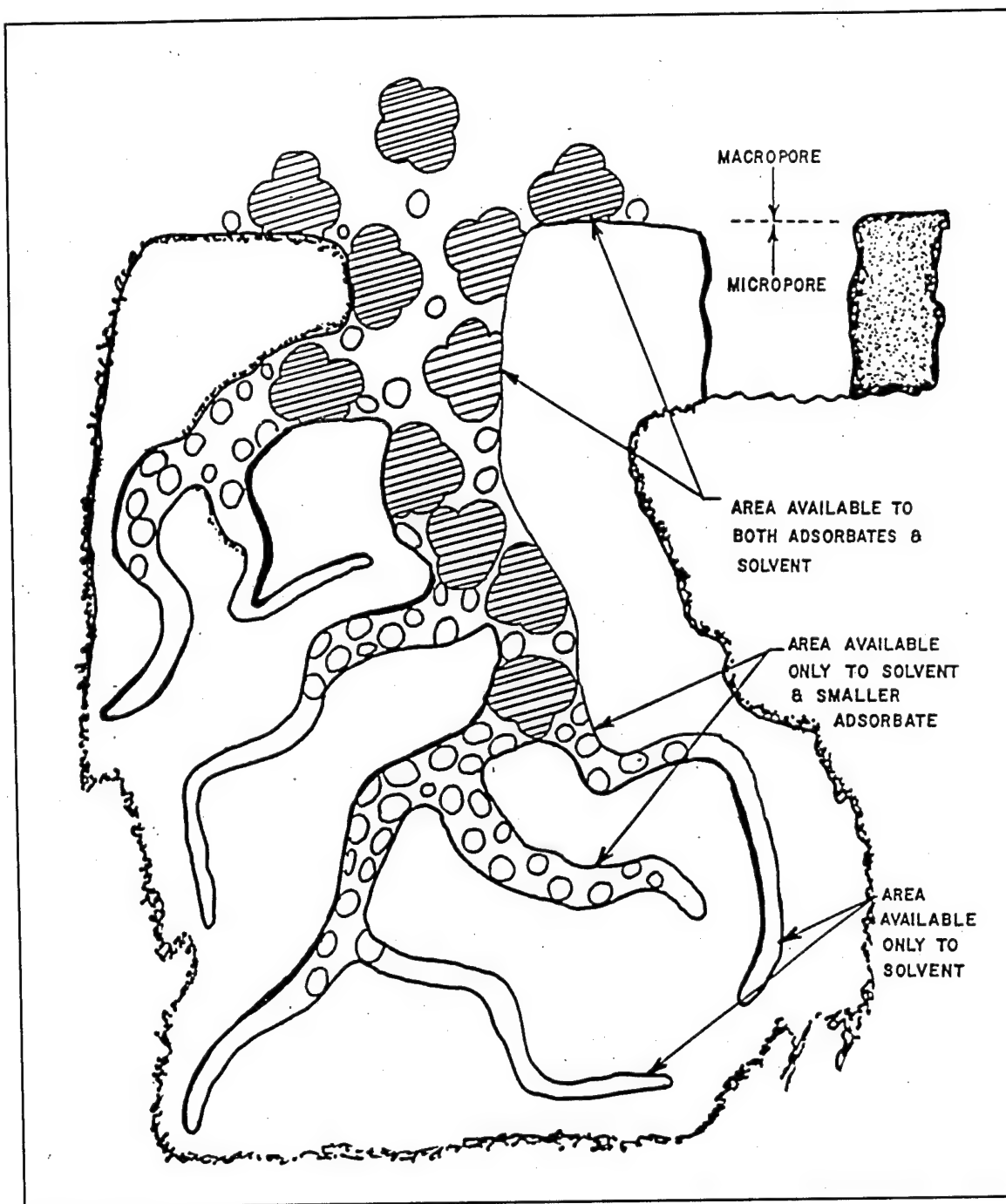
Figure 3. Illustration of pores within a carbon granule (Bricka and Fleming 1995)

Generally, the adsorption capacity will increase with the increased molecular weight of the adsorbate as a homologous series is ascended. A homologous series is a series in which each member differs from the next member by a constant amount (Morrison and Boyd 1987). For example, butane contains one carbon and two hydrogens more than propane, which contains one carbon and two hydrogens more than ethane. Isomeric structure also affects adsorption capacity. For instance, adsorption capacity will decrease for the position

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of substitution of hydroxy and amino-benzoic acids in the order ortho, para, and meta and decrease with branching (Belfort 1980). Belfort also states that "despite all the attempts at correlating the extent of adsorption with these variables, not one parameter has emerged in predicting the dominant effect of adsorption."

Competitive adsorption

Adsorption of a particular adsorbate can be highly affected by the presence of other more strongly adsorbed adsorbates. No information regarding the effects of the combinatorial presence of RDX, TNB, TNT, and HMX were found, but the available information for RDX and TNT indicates competitive adsorption may occur. Cheremisinoff and Ellerbusch (1978) report the adsorption capacity of Calgon Filtrasorb 400 for RDX was reduced approximately 40 percent by the presence of TNT since TNT is more strongly adsorbed. Faust, Aly, and Osman (1987) compare the effects of single-solute adsorption of phenol and dibenzenesulfonate (DBS) to adsorption of equal amounts of each adsorbate in the same test. In adsorption tests using both adsorbates in the same solution, the results indicated that phenol adsorption was reduced 24 percent and DBS adsorption reduced by 12 percent compared with adsorption for each component in single-solute systems. However, the total capacity of the adsorbent for the total adsorbate (DBS and phenol in the same solution) increased over the capacity of the single component systems.

Properties considered in selection of adsorbents

Some of the properties considered in the selection of adsorbents for this study were product of formation (feed to the production process), available surface area, and pore-size distribution. The macroreticular resins selected for evaluation are formed by pyrolyzation of polymers and have similar properties to that of carbon. Some of the products from which carbons may be formed include bituminous coal, coconut shell, lignite, wood, and pulp mill residue. The product of formation influences the properties of the adsorbent and may make it more suitable for particular applications (Faust, Aly, and Osman 1987). For example, coconut shell carbons have considerably finer pore-size distribution and higher apparent density than carbon produced from paper mill waste. Apparent density is the measure of a carbon's regenerability. The higher the apparent density, the greater the regenerability.

The degree of pyrolyzation affects the available surface area and thus adsorptive capacity. The surface area of an adsorbent correlates directly with the amount of area available for adsorption and includes macropores, mesopores, and micropores (see Figure 3). Macropores are generally considered as those pores greater than 1,000 Å, while micropores range between 10 and 1,000 Å (Cheremisinoff and Ellerbusch 1978). The molecular sizes of most organic compounds are from approximately 2 to 10 Å. The most tenacious adsorption occurs in pores that are barely large enough to admit the adsorbing

molecules (USEPA 1971). The smaller the pores with respect to the adsorbate, the greater the forces of attraction. The typical method for determining the surface area of adsorbents is the nitrogen adsorption isotherm by the Brunauer, Emmett and Teller Method (BET Method) (USEPA 1971). Surface area is generally expressed in square meters per gram of adsorbent.

Adsorption studies are generally conducted using pulverized carbon to decrease the time necessary to complete the isotherm by decreasing the amount of time required to reach equilibrium. However, pulverization does not affect the available surface area. The available surface area is only increased approximately 1 percent due to pulverization since most of the surface area is contributed by the pore walls rather than by the external surface of the carbon particle (Cheremisinoff and Ellerbusch 1978). The granular version of the adsorbents and the corresponding powdered version are presented in Table 1. Throughout this report, the granular version of the adsorbent will be referenced, but all phases of the study were conducted using powdered adsorbents, pulverized to the point that 95 percent by weight of the adsorbent would pass through a 325 mesh screen.

Table 1
Vendor Trade Names for Granular and Powdered Adsorbents

Granular Trade Name	Powdered Trade Name
Carbons	
Calgon Filtrasorb 400	Calgon WPH
Calgon Filtrasorb 200	Calgon WPL
American Norit Hydrodarco 4000	American Norit Hydrodarco B
Westates CC-601	Westates CC-601
Calgon Coconut Shell GAC	Calgon Coconut Shell PAC
American Norit ROW 0.8	American Norit D-10
Carbonaceous Resins	
Ambersorb 563	Not Applicable
Ambersorb 572	Not Applicable
Polymeric Resin	
Amberlite XAD-4	Not Applicable
Organophilic Clays	
Clarion PM-100	Clarion RM-10
Biomin EC-100	Biomin PT1E

Another property considered in the selection of adsorbents is the iodine number. Iodine number is a measure of a carbon's ability to adsorb low molecular weight compounds (molecular weights of RDX, TNB, TNT, and HMX are 222.3, 213.1, 227.1, and 296.2 g/mol, respectively). The iodine number can also be correlated with the total area of pores having openings less than 10 Å in diameter (USEPA 1971). Iodine number is determined by adsorbing iodine onto carbon and determining the adsorption capacity for iodine when the residual iodine concentration is 0.02 Normal. Methods for iodine number determination are presented in American Society of Testing and Materials (ASTM) D 4607-86 (ASTM 1994). Iodine number is generally reported for carbon, but was not presented in available vendor literature for the Ambersorb resins. Molasses number is a number correlated with the ability to adsorb high molecular weight compounds and correlates to the total area of the pores having openings greater than 10 Å in diameter.

Activation

The amount of impurities present varies depending on the formation product. They are generally removed during the activation process. Carbon materials are activated in three steps: (a) removal of all water, (b) conversion of organic matter to elemental carbon, driving off the noncarbon portion, and (c) burning off tars and pore enlargement (activation). Activation also affects pore-size distribution. Faust, Aly, and Osman (1987) compare steam activation for two carbons. Activation of one carbon for 1 hr longer resulted in an 83-percent increase in surface area and widening of some more narrow pores.

Properties specific to macroreticular resins

Macroreticular resins have many of the same properties as carbons but are different. For the macroreticular resins, micropores are produced during pyrolysis. The nature of the micropores and their surface characteristics are controlled by the pyrolysis conditions. The surface area contributed by macropores and mesopores is controlled by pyrolysis temperature and atmospheric conditions. The pore-size distribution is also controlled during manufacturing by varying the level of crosslinking between the compounds composing the resin. For example, in the case of Ambersorb 563 and 572, the pore-size distribution is controlled by crosslinkage of styrene and divinyl-benzene. Another important feature of macroreticular resins is the absence of ionic groups, which means the resins can serve as hydrophobic adsorbents capable of removing hydrophobic adsorbates from solution via van der Waals interactions (Faust, Aly, and Osman 1987).

Polymeric adsorbents are produced by crosslinking polymers without pyrolyzation. They derive their adsorptive properties from their macroreticular structure (containing both a continuous polymer phase and a continuous pore phase), high surface area, and the aromatic nature of their surface (Rohm and Haas technical bulletin).

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Properties specific to organophilic clays

The mechanism of contaminant removal in the area of organophilic clays is by partitioning of the contaminant onto the clay surface. Figure 4 illustrates clay platelets. As organics are adsorbed, the platelets spread further apart. Clay platelets have a much larger surface area than GAC, resulting in much larger capacity to remove organics with low solubility. Clays form a phase with the water, derived from the hydrocarbon tail attached to the clay.

Adsorbate properties considered in selection of adsorbents

Adsorbate properties strongly affect the effectiveness of adsorbents. The main adsorbate properties considered in the study were the initial concentrations and the solubilities of RDX, TNB, TNT, and HMX. When equilibrium is achieved in adsorption systems, the adsorbate is desorbed and adsorbed at the same kinetic rate, and a state called adsorption equilibrium exists. Adsorption effectiveness generally increases with increased adsorbate concentration because in order to reach equilibrium, more adsorbate is adsorbed onto the adsorbent. Adsorbent effectiveness increases as the solubility of the adsorbate decreases because the equilibrium driving forces favor the adsorbent phase, not the water phase. The solubilities of RDX, TNB, TNT, and HMX are 50, 350, 130, and 5 mg/ℓ, respectively. The chemical structures of RDX, TNB, TNT, and HMX are illustrated below.
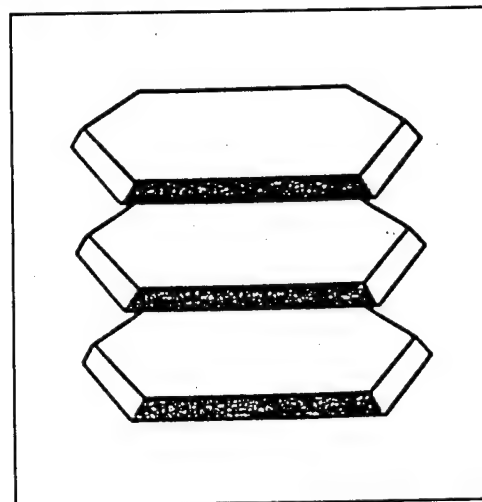
Figure 4. Illustration of clay platelets (CETCO technical data sheet)

HMX Molecular Composition
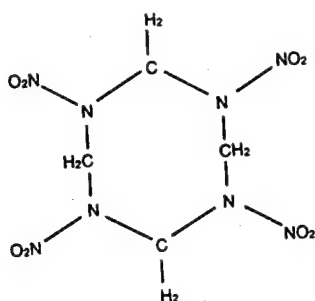
RDX Molecular Composition
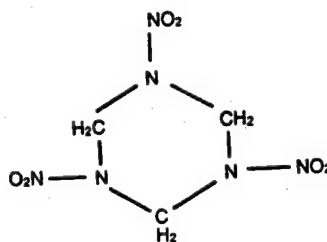
TNB Molecular Composition
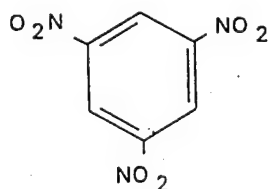
TNT Molecular Composition
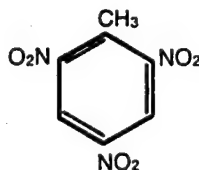
Previous Studies

Wujcik et al. (1992) evaluated removal of RDX and TNT from waters collected from the Milan Army Ammunition Plant (MAAP) in Milan, TN. Batch isotherm tests revealed that RDX and TNT levels were reduced from 549.1 $\mu g/\ell$ RDX and 734 $\mu g/\ell$ TNT to "not determinable" for all carbon dosages tested. In the next phase of study, column studies were conducted to determine the dynamics of RDX and TNT adsorption. Based upon column data, the carbon capacity for RDX was 0.158 lb[1] RDX per pound of Atochem, Inc., carbon and 0.122 lb RDX per pound Calgon Filtrasorb 300. The capacity for TNT was 0.338 lb TNT per pound Atochem, Inc., carbon and 0.330 lb TNT per pound Calgon Filtrasorb 300 carbon. Atochem, Inc., carbon treated 733 bed volumes of TNT to an effluent level of 0.769 $\mu g/\ell$, and Calgon Filtrasorb 300 treated 733 bed volumes of MAAP water to 1.30 $\mu g/\ell$ TNT. In another study of MAAP waters by Wujcik, Lowe, and Marks (1990), he presented data for removal of RDX and TNT in isotherm form. The isotherms generated during that study are presented as Figures 5 and 6 for RDX and TNT, respectively. For the RDX isotherms, three of the GAC isotherms (Calgon Filtrasorbs 200, 300, and 400) could not be completed because the analytical results were below the detection limit at dosages higher than 200 mg/ℓ carbon. Similarly, all isotherms for TNT were incomplete because dosages higher than 200 mg/ℓ yielded results in the liquid phase less than the detection limit. After review of these data, a modified method for testing smaller dosages on CAAP waters was used in this study so that isotherms could be obtained for the CAAP waters and will be discussed in the "Materials and Methods" section of this report.

Castorina, Haberman, and Sharma (1982) studied adsorption of TNT and found that 0.52 g TNT were adsorbed per gram of Calgon Filtrasorb 300, representing approximately two-thirds surface area coverage of the Filtrasorb 300 (concepts of adsorption to be discussed in "Materials and Methods"). In Castorina's article on TNT adsorption, he indicates that TNT replaces RDX from the adsorbed state and TNT remains adsorbed, causing RDX to be released. Schulte, Hoehn, and Randall (1973) evaluated Westvaco Nuchar Activated Carbon, type WV-G for removal of TNT and found the saturation capacity of TNT-spiked distilled water solutions was approximately 0.68 g TNT per gram carbon at an initial concentration of 82.5 mg/ℓ TNT.

Hinshaw et al. (1987) evaluated Calgon Filtrasorb 200, 300, and 400, Westvaco Nuchar WV-G, and Witco Witcarb 950 for removal of RDX, HMX, TNT, and 2,4-DNT. The influent concentrations of RDX, HMX, TNT, and 2,4-DNT were approximately 23.3, 4.58, 61.8, and 0.779 mg/ℓ, respectively. The optimal carbon for removal of RDX, HMX, TNT, and 2,4-DNT was Witcarb 950. The saturation capacity using Witcarb 950 was

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[1] To convert pounds (mass) to kilograms, multiply by 0.4535924.
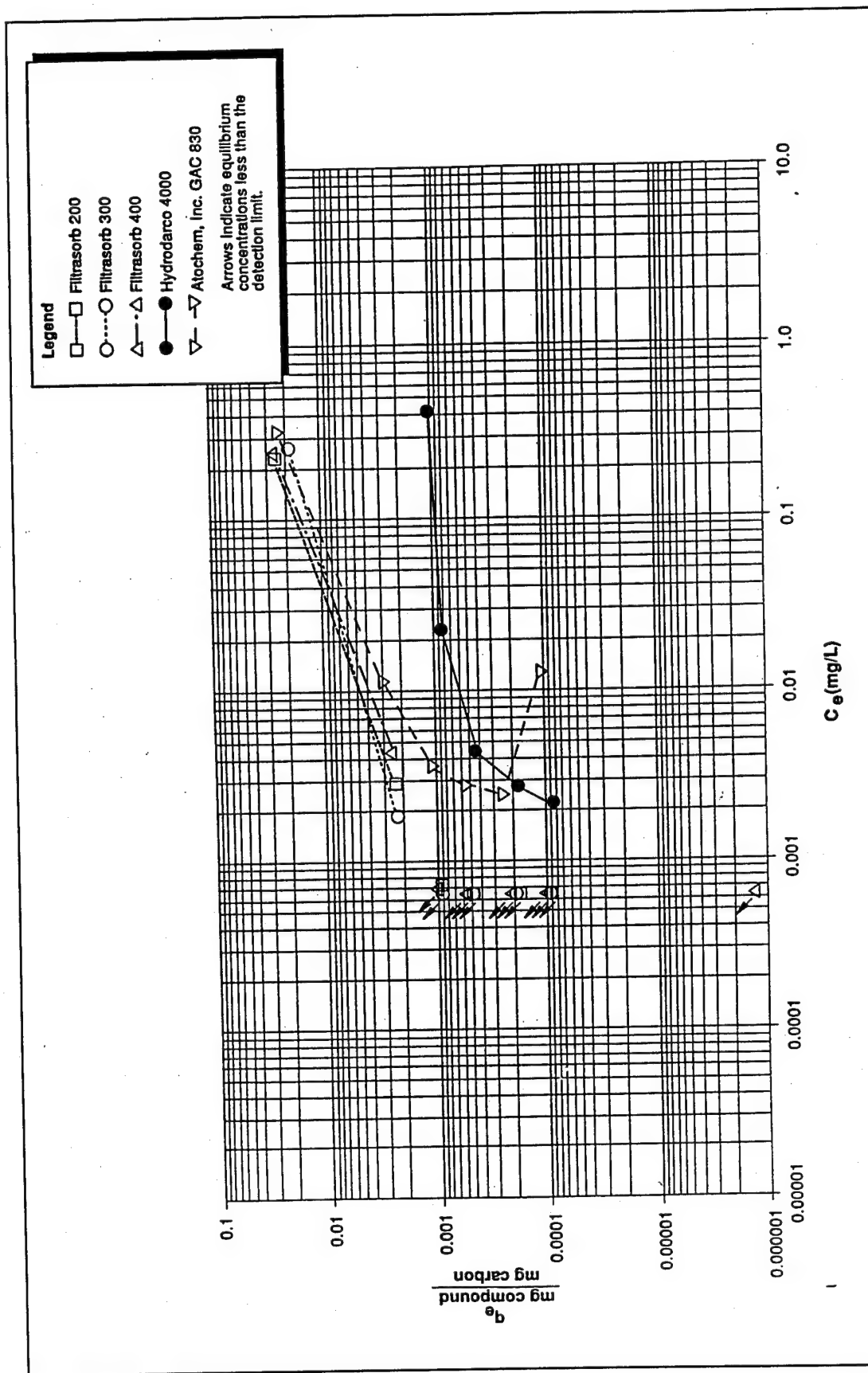
Figure 5. Wujcik isotherm for RDX (Wujcik, Lowe, and Marks 1990)
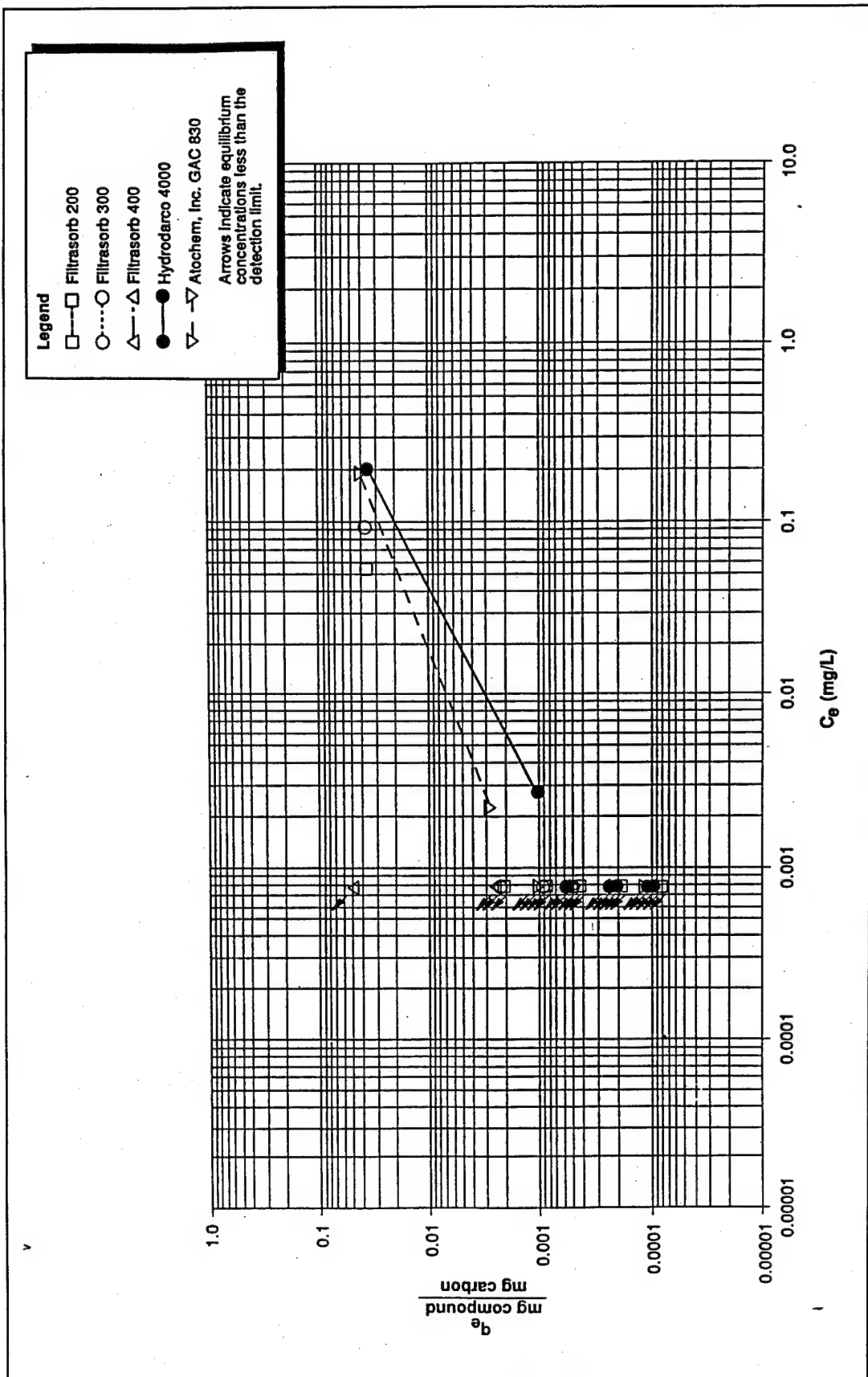
Figure 6. Wujcik isotherm for TNT (Wujcik, Lowe, and Marks 1990)

0.56 mg TNT/g, 0.066 mg RDX/g, 0.024 mg HMX/g, and 0.017 mg 2,4-DNT/g.

Cheremisinoff and Ellerbusch (1978) reports the capacity of Calgon Filtrasorb 400 (F-400) was 0.125 g RDX per gram of carbon in studies conducted by Vlahakis (1974) on munitions-contaminated wastewater. However, the capacity of F-400 was significantly reduced to 0.076 g RDX per grams of carbon by the presence of TNT in the water. Other studies discussed by Cheremisinoff report 80- to 90-percent removal of RDX and TNT from solutions with initial concentrations of approximately 40 mg/ℓ TNT and 23 mg/ℓ RDX.

Stevens et al. (1975) evaluated Calgon Filtrasorb 300 in column studies for removal of RDX and TNT from Burlington Iowa Army Ammunition Plant waters. The influent concentrations of RDX and TNT were approximately 89 and 108 mg/ℓ, respectively. The adsorbent capacity for RDX and TNT was 0.074 mg RDX per gram Calgon Filtrasorb 300 and 0.125 mg TNT per gram Calgon Filtrasorb 300 at an effluent concentration of 1 mg/ℓ TNT and 25 mg/ℓ RDX. Stevens et al. (1975) compared the results of the Calgon Filtrasorb 300 study with Amberlite XAD-4 for removal of TNT (108 mg/ℓ) and RDX (89 mg/ℓ). The data presented in the study showed that Amberlite XAD-4 was more effective than Filtrasorb 300 in removal of TNT and less effective for removal of RDX. The adsorption capacities of Amberlite XAD-4 were 0.435 g TNT adsorbed per gram of Amberlite XAD-4 (3 1/2 times that of Filtrasorb 300) and 0.057 g RDX per gram of Amberlite XAD-4 (23 percent less efficient than Filtrasorb 300).

Balasco, Cheng, and Field (1987) describe a study on regeneration of explosive-laden carbons and present data from several Army ammunition plants (AAPs). The adsorption capacities of carbons for explosives from a number of those sites are presented in Table 2. The adsorption capacities varied significantly probably due to a number of factors including concentrations of each explosive present and solubility and molecular size of the explosives.

Table 2 Adsorption Capacity of Carbons for Explosives in Wastewaters from AAPs (Balasco, Cheng, and Field 1987)			
AAP	Explosive	Carbon	Adsorption Capacity, lb/lb
Radford	TNT/DNT	F-400	0.19
Lone Star	TNT RDX	HD 4000	0.125 0.090
Kansas	RDX	NA[1]	0.300
Joliet	TNT	Witco/Calgon	0.041
[1] Indicates not available.			

No data were available on the use of organophilic clays for removal of RDX, TNB, TNT, or HMX. The efficiency of organophilic clays is dependent on the solubility, or such as the case with explosives, insolubility of the adsorbate that was the premise for their selection for evaluation.

The most common regeneration method for carbon is thermal oxidation using a multiple hearth furnace (Faust, Aly, and Osman 1987). Temperatures in the furnace generally range from 1,600 to 1,800 °F.[1] The exit temperature from the furnace ranges from 600 to 700 °F. In multiple hearth furnace operations, the loss of carbon capacity due to oxidation and attrition is a significant factor in the overall economics of carbon water treatment. The best method of determination of carbon losses is through measurement of carbon dioxide in the exhaust gas by gas chromatography. Gas analyses can then be used to calculate the loss of carbon by reaction with other components (Cheremisinoff and Ellerbusch 1978).

Castorina, Haberman, and Sharma (1982) evaluated regeneration of Calgon Filtrasorb 300 carbon using acetone as the solvent. Using virgin carbon, the adsorption capacity of Calgon Filtrasorb 300 was 0.48 g TNT per gram Filtrasorb 300. Castorina, Haberman, and Sharma (1982) evaluated multiple regenerations of TNT-loaded carbon and found the adsorption capacity decreased with each successive cycle (adsorption and desorption represent one cycle). The results of their study showed TNT adsorption decreased as the cycles went from one to five and were 0.48, 0.45, 0.37, 0.24, and 0.22 g TNT/g Calgon Filtrasorb 300, respectively. After the fifth solvent regeneration cycle, the adsorption capacity of the regenerated carbon was less than half that of virgin carbon.

Stevens et al. (1975) evaluated Amberlite XAD-4 for its removal of TNT and followed by regeneration of the XAD-4 using acetone. The results showed an approximately 5.6-percent reduction in TNT removal efficiency in the first cycle and 14.6-percent reduction in TNT removal during the second regenerative cycle.

Regeneration of the carbonaceous resins is generally accomplished by solvent regeneration or steam regeneration. Alcohols such as methanol, ethanol, or isopropanol and other organic solvents such as acetone are commonly used. Solvent regeneration is generally used when high levels of contamination are present in the water. Steam regeneration is usually the method of choice (Neely and Isacoff 1982) because tests conducted using steam versus solvent regeneration indicated resins regenerated by steam were more effective at further treatment than solvent-regenerated resins.

In some cases, it may not be desirable to regenerate the adsorbent. The loading, hauling, and regeneration of spent and reactivated adsorbents may not

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[1] To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use the following formula: $C = (5/9) (F-32)$.

be as cost-effective as the use of adsorbents on a throwaway basis, particularly for small plants. In determining whether adsorbent regeneration or disposal is the most cost-effective, detailed cost analysis should be performed on a site-by-site basis.

3   Materials and Methods

Groundwater Collection

WES personnel collected water for the bench-scale evaluations from CAAP Well Number 23. CAAP Well 23 water was expected to contain concentrations of RDX, TNB, TNT, and HMX similar to concentrations in groundwater at the CAAP boundary. Approximately 275 gal (1,040.98 ℓ) of CAAP water were shipped to the WES in five 55-gal (208.19-ℓ) drums and maintained at 4 °C for the duration of the study.

Selection of Adsorbents

The carbons selected for evaluation were Calgon F-400, Calgon Filtrasorb 200 (F-200), Calgon Coconut Shell Carbon, Hydrodarco 4000, American Norit ROW 0.8, and Westates CC-601. The carbonaceous adsorbents selected for adsorption were Ambersorb 563 and Ambersorb 572. One polymer, Rohm and Haas XAD-4, and two organophilic clays, Biomin EC-100 and Clarion PM-100, were selected for evaluation. All of the aforementioned adsorbents represent the granular version of the adsorbent. The powdered version trade name of each adsorbent is presented in Table 1. The difference between the Ambersorb resins and XAD-4 is that the Ambersorb series represents pyrolyzed polymers and XAD-4 is unpyrolyzed. The suppliers and their addresses for each adsorbent are presented in Table 3. The properties of each adsorbent are presented in Table 4. The costs of the adsorbents used during the preliminary tests are provided in Table 5.

Description of carbons selected

Six carbons were selected and differed mainly by the parent product from which they were manufactured. Because of the variability in the product of formation, the properties of the carbons that were evaluated were variable. Two bituminous coal products, Calgon F-400 and F-200, and two coconut shell products, Calgon CSC and Westates CC-601 CSC, were selected for

Table 3
List of Materials and Addresses of Vendors for Preliminary Tests

Materials	Vendor
Coconut Shell Carbon 12x30 Granule F-200 F-400	Calgon Carbon Pearl River Plant P.O. Box 620 Pearlington, MS 39572 (601) 533-7171
Ambersorb 563 Ambersorb 572 XAD - 4	Rohm and Haas Bldg. 20, Suite 100 727 Norristown Road Spring House, PA 19477 Fax: (215) 619-1613 (215) 641-7478
Hydrodarco 4000 ROW 0.8 (D-10)	American Norit 1050 Crown Pointe Parkway Suite 1500 Atlanta, GA 30338 (800) 641-9245
Westates CC-601	Westates Carbon 2130 Leo Avenue Los Angeles, CA 90040 (213) 722-7500
Biomin EC-100	Biomin, Inc. P.O. Box 20028 741 W. Oakridge Ferndale, MI 48220 (810) 544-2552
Clarion PM-100	Pressure Products 406 South Royal Street Mobile, AL 36603 (205) 438-1001

evaluation. American Norit ROW 0.8 and Hydrodarco 4000 were selected for evaluation of extruded and lignite carbons, respectively.

Description of carbonaceous resins selected

Ambersorb 563 is a carbonaceous adsorbent produced by pyrolyzation of macroreticular sulfonated styrene/divinylbenzene copolymer. It is the most hydrophobic of Rohm and Haas resins. A water adsorption isotherm illustrating the hydrophobic nature of Ambersorb 563 is presented in Figure 7. Ambersorb 563 adsorbs significantly less water than F-400 in the water adsorption isotherm. Therefore, it may adsorb more of the RDX, TNB, TNT, and HMX since they are relatively insoluble in water. Ambersorb 563 also has significantly more surface area in the macropore and mesopore region, and Rohm and Haas literature indicates it may treat up to five times the bed volumes of F-400 in certain applications. Rohm and Haas literature also states that Ambersorb 563 can treat water at a higher flow rate than GAC

Table 4
Properties of Carbon and Carbonaceous Resins

| Adsorbent | BET Surface Area[1] m²/g | Pore-Volume Distribution, cm³/g | | | Iodine No. mg/g |
		Macro	Meso	Micro	
Calgon CSC	1,150-1,250	NA	NA	NA	1,200
F-200	900	NA	NA	NA	900
F-400	950	0.04	0.09	0.48	1,000
XAD-4	800	NA	NA	NA	NA
Hydrodarco 4000	625	0.93[2]	NA	NA	600
American Norit ROW 0.8	550	1.0[2]	NA	NA	575
Westates CC-601	1,100	NA	NA	NA	1,100
Ambersorb 563	550	0.23	0.14	0.23	NA
Ambersorb 572	1,100	0.24	0.19	0.41	NA

Note: NA = Not available.
[1] Surface area for pulverized carbon = surface area of GAC. Pulverization does not affect surface area (Cheremisinoff and Ellerbusch 1978).
[2] Total pore volume available.

Table 5
Costs of Each Material Evaluated in Preliminary Tests

Material	Cost, per lb
Carbons	
F-200	$1.00
F-400	$0.95
Calgon Coco. Shell	$1.69
Hydrodarco 4000	$1.00
American Norit ROW 0.8 (D-10)	$0.80
Westates CC-601	$1.00
Polymeric Resin	
XAD-4	$11.16
Carbonaceous Resins	
Ambersorb 563	$32.38
Ambersorb 572	$47.56
Organophilic Clays	
Biomin EC-100	$1.10
Clarion PM-100	$2.25

systems. Ambersorb 572 is the most hydrophilic pyrolyzed adsorbent and has surface characteristics similar to GAC. Ambersorb 572 was selected because it has much larger surface area than F-400 or Ambersorb 563 and may also treat much higher bed volumes than F-400.

Selection of a polymeric resin

Rohm and Haas XAD-4 is a crosslinked polymeric adsorbent that derives its adsorptive properties from its macroreticular structure, high surface area, and the aromatic nature of its surface. XAD-4 can be used to adsorb hydrophobic molecules from polar solvents or volatile organic compounds from vapor streams. The pore-size distribution of XAD-4 makes it
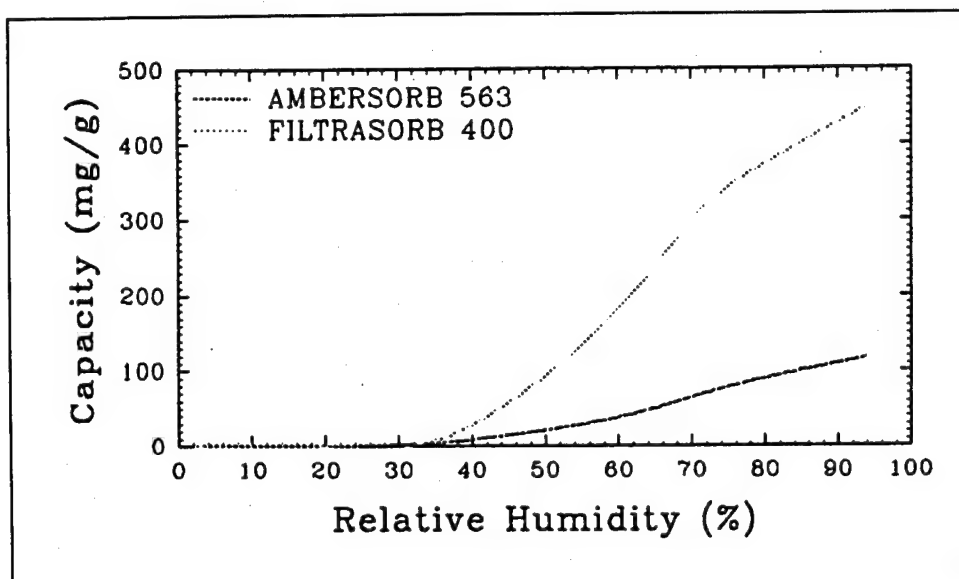
Figure 7.   Water adsorption isotherm for F-400 and Ambersorb 563 (Rohm and Haas technical data sheet)

suited for adsorption of relatively low molecular weight organics such as RDX, TNB, TNT, and HMX.

Selection of organophilic clays

Biomin EC-100 and Clarion PM-100 were selected for the organophilic clay evaluations. Biomin EC-100 is a blend of bentonite and anthracite, and vendor literature indicates removal of contaminants at 20 to 40 percent higher efficiency than GAC. The literature indicated Biomin EC-100 removes 40 to 60 percent of its weight in oil and grease, where GAC removes 10 to 15 percent. Clarion PM-100 is a blend of 30-percent active (proprietary) adsorbent and 70-percent anthracite filter media. Clarion PM-100 literature indicates adsorption of up to 60 percent of its weight of organics.

Preparation of Test Containers

Samples were prepared and testing conducted in 820-ml glass bottles with Teflon-lined caps. Each bottle used for testing was washed according to methods described in ASTM D 3694 (ASTM 1994), with modifications. Each container was rinsed with 100 ml of acetone, then rinsed three times with 100-ml portions of distilled water. After this point, the lip of the bottles was not touched by any foreign objects. If protocol was broken, the entire procedure was repeated. The bottles were then heated to 325 °C for 4 hr. After 4 hr, the bottles were removed from the oven, capped with aluminum foil, taped to prevent breakage or photolysis, and placed in storage until ready for use.

Preparation of Adsorbents

American Norit Hydrodarco 4000, American Norit ROW 0.8, Calgon CSC, Calgon F-400, Calgon F-200, and Westates CC-601 were prepared by oven-drying at 150 °C according to procedures described in ASTM D 2867 (ASTM 1994). When the weight of the carbons was constant, the carbon was considered sufficiently dry.

Ambersorb 563 is extremely hydrophobic and required a hydration period of 4 days before use according to methods described by Rohm and Haas (Rohm and Haas 1994). At the completion of the hydration period, Ambersorb 563 was ready for use. Ambersorb 572 is sufficiently hydrophilic and did not require hydration prior to use.

Clarion PM-100 and Biomin EC-100 did not require special handling procedures before use.

Sample Preparation

On the day before testing, approximately 20 ℓ of CAAP water was removed from cold storage and allowed to reach room temperature overnight. The 20 ℓ of CAAP water was pumped into a 20-ℓ amber-coated bottle using a Masterflex model No. 7553-20 peristaltic pump with Teflon tubing. An amber-coated bottle was used to help prevent photolysis of the explosives, and Teflon tubing was used to minimize adsorption of explosives during pumping. Prior to addition of the adsorbent and CAAP water to the test bottles, displacement tests were conducted to determine the appropriate amount of adsorbent to add to each bottle. Addition of high quantities of adsorbent can result in significant displacement of water (Schneiter, Drafun, and Kalinowski 1985). Displacement tests were performed according to procedures described by Schneiter et al. (1985). Each displacement test was conducted using 5 g of adsorbent in 1,000 ml of distilled water. The results of the displacement tests are presented in Table 6. For CAAP waters, relatively low dosages of adsorbent were required for treatment below detection limits of 0.2 $\mu g/\ell$, resulting in negligible displacement of the water by the adsorbent. For example, displacement tests in a 1-ℓ volumetric flask were conducted on Ambersorb 563. Approximately 5 g of Ambersorb 563 and 1,000 ml of water were added to the flask. The volume of water measured above the 1,000-ml mark on the flask was the volume of water displaced by the 5 g of adsorbent. The 5 g of Ambersorb 563 displaced approximately 0.5 percent of the water. The percentage displacement of the water by the adsorbent was negligible for testing purposes in this study.

Depending upon the dosage used, adsorbents were weighed on an A & D FR 200 MKII balance or a modified method (discussed below) was used. The dosage for the preliminary tests and equilibrium time determination tests was 250 mg/ℓ, and the adsorbent was weighed into the sample bottles using the

Table 6	
Amount of Water Displaced by 5 g Absorbent in 1,000 ml Water	
Adsorbent	**Water Displaced, ml[1]**
Coconut Shell Carbon	1
Ambersorb 563	5
Ambersorb 572	5
Hydrodarco 4000	7
Westates CC-601	8
ROW 0.8	5
Calgon F-400	2
Calgon F-200	8
Biomin EC-100	7
Clarion PM-100	8
[1] 5 g of adsorbent in 1,000 ml water.	

balance. The dosages selected for the isotherm tests were 25, 50, 100, and 250 mg/ℓ. Two stock carbon slurries were prepared for this phase of the study. One slurry contained 4.1 g of the adsorbent in a 1-ℓ volumetric flask, and the other contained 41 g of adsorbent in a 1-ℓ volumetric flask. To obtain dosages of 25, 50, and 100 mg/ℓ, 5, 10, and 20 ml of the 4.1 g adsorbent slurry, respectively, were pipetted into each 820-ml bottle. To obtain a 250-mg/ℓ dosage, 5 ml of the 41 g adsorbent slurry were pipetted into the 820-ml bottles.

Before actual testing, a method accuracy evaluation test was performed to test the accuracy of the modified method for dosing the carbon into the test bottles. The 4.1 g adsorbent and 41 g adsorbent slurries were prepared and tested to ensure that the proper amount of adsorbent was drawn into the pipette to attain the required dosage. The method accuracy evaluation involved weighing the carbon on the A & D FR 200 MKII balance, transferring the carbon to a 1-ℓ volumetric flask, filling the flask with distilled water, and stirring for 10 min. Then, 5, 10, and 20 ml of the 4.1 g slurry and 5 ml of the 41 g slurry, corresponding to 25-, 50-, 100-, and 250-mg/ℓ dosages, respectively, were filtered onto a preweighed filter and oven-dried to determine whether the proper amount of carbon had been pipetted. The results of the method accuracy evaluation tests are presented in Table 7. A Masterflex model No. 7553-20 peristaltic pump with Teflon tubing was used to pump CAAP water from the 20-ℓ amber bottle to the test bottles. The tubing was held to the glass of the test bottle and the liquid allowed to flow down the side to help prevent turbulence. After the adsorbent was pipetted/weighed into the test bottle, the test bottle was totally filled to eliminate headspace.

Preliminary tests

A list of the adsorbents and dosages tested in the preliminary tests is presented in Table 8. The tests were conducted in batch for 24 hr. Influent samples were the first samples collected into 1-ℓ amber bottles and were collected in triplicate for preliminary testing and duplicate for the remainder of the tests. Method blanks were also collected to determine the amount of losses due to handling procedures during testing. Method blanks were subjected to the same procedures as the adsorbent/CAAP water test samples but

Table 7
Results of Method Accuracy Evaluation Tests

Carbon	Replicate	Dosage, mg/ℓ	Method Percent Error	Average Percent Error
Calgon F-400	1	25	4.4	
	2	25	9.3	
	3	25	9.3	7.7
	1	50	4.6	
	2	50	2.7	
	3	50	5.4	4.2
	1	100	5.7	
	2	100	9.8	
	3	100	0.7	5.4
	1	250	1.8	
	2	250	0.1	
	3	250	1.7	1.2
Westates CC-601	1	25	8.3	
	2	25	4.9	
	3	25	4.9	6.0
	1	50	1.5	
	2	50	14.6	
	3	50	20.2	12.1
	1	100	6.0	
	2	100	9.6	
	3	100	12.6	9.4
	1	250	8.7	
	2	250	15.9	
	3	250	1.0	8.5
American Norit ROW 0.8	1	25	0.5	
	2	25	8.3	
	3	25	3.9	4.2
	1	50	1.2	
	2	50	3.7	
	3	50	7.8	4.2
	1	100	8.4	
	2	100	8.0	
	3	100	6.2	7.5
	1	250	12.4	
	2	250	11.5	
	3	250	11.5	11.8

Table 8
List of Preliminary Tests[1]

Batch No.	Adsorbent	Dosage, mg/ℓ
1	Influent	NA[2]
	Method Blank	NA
	Hydrodarco 4000	250
	Coconut Shell PAC	250
	Calgon F-400	250
	Calgon F-200	250
2	Influent	NA[2]
	Method Blank	NA
	Ambersorb 563	125
	Ambersorb 572	125
	Amberlite XAD-4	3,000
3	Influent	NA[2]
	Method Blank	NA
	American Norit ROW 0.8	250
	Westates CC-601	250
	Biomin EC-100	3,000
	Clarion PM-100	3,000
4	Ambersorb 563	250
	Ambersorb 572	250

[1] Samples tested in duplicate.
[2] Samples tested in triplicate.

contained only CAAP water (i.e., no adsorbent). Influent and method blank samples were collected for Batches 1-3. Batch 4 represents additional samples not identified in the scope of work, and the number of samples available for that series of tests was limited so influent and method blank samples were not collected. Preliminary, equilibrium time determination, isotherm tests, and confirmation tests were evaluated in duplicate. Since the test bottle capacity was 820 ml, three bottles were prepared, and the two 1-ℓ amber sample bottles were filled to one-third full using the three 820-ml test bottles.

At the completion of the tumble time, the test bottles were removed from the tumblers, and suspended adsorbent was removed using in-line stainless steel filters. Samples were collected in precleaned 1-ℓ amber bottles, stored at 4 °C overnight, and submitted to the ECB for analysis the next day.

Equilibrium time determinations

Basically, the same sample handling procedures used during the preliminary evaluations were used for equilibrium time determinations. The only variation was that duplicate influent samples were collected instead of triplicate influent samples. The contact times tested were 0, 1, 2, 4, 8, and 24 hr, and the adsorbent dosage was 250 mg/ℓ. A 0-hr sample represented removal by the adsorbent without tumbling in the TCLP-type tumblers and indicated that removal occurred in approximately 10 min, the time required to pump CAAP water into and out of the bottles.

Isotherm testing

The same sample handling procedures were used as in the previous tests, collecting duplicate influent, method blank, and test samples. The only exception was the procedure for addition of adsorbent, using the modified method previously discussed. The dosages evaluated were 25, 50, 100, and 250 mg/ℓ.

Confirmation testing

After the results of the isotherm tests were received, confirmation tests were performed to confirm the results of the isotherm tests. The same procedures for isotherm testing were used for the confirmation tests, basically repeating the isotherm tests but preparing one replicate for each dosage of each adsorbent in one batch.

Regeneration testing

Regeneration tests involved treating 20 ℓ of CAAP water with each carbon. A large batch of CAAP water was treated so that a sufficient mass of carbon was recovered with which to perform additional adsorption tests after regeneration. For example, to evaluate the highest carbon dosage, 250 mg/ℓ, 0.205 g of carbon was placed into the 820-ml sample bottle. After adsorption the first time, before regeneration, it would be difficult to recover 0.205 g of carbon from the sample bottle. Using a 20-ℓ amber-coated bottle, 5-g portions of each adsorbent were added to the 20 ℓ of CAAP water for a dosage of 250 mg/ℓ. Figure 8 represents a schematic diagram of the regeneration phase of the study.

Influent samples were collected and the carbon and CAAP water were mixed on a Fisher Scientific Model 128 stir plate for 24 hr, the carbon was filtered from the bottle and retained for regeneration, and the treated CAAP water analyzed for RDX, TNB, TNT, and HMX. The explosives-loaded carbon was mixed with 200 ml of acetone for 24 hr. The carbon was filtered from the acetone and dried in a 100-ml/min nitrogen-purged oven at 140 °C

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┌─────────────────────────────────┐
│    Collected influent samples   │
└─────────────────────────────────┘
                 │
                 ▼
┌─────────────────────────────────────────────┐
│  Adsorb explosives in 20 liter amber bottles using Calgon │
│   F-400, American Norit ROW 0.8, and Westates CC-601      │
└─────────────────────────────────────────────┘
                 │
                 ▼
           ┌──────────┐
           │  Filter  │
           └──────────┘
            │        │
    ┌───────┘        └────────┐
    ▼                         ▼
┌─────────────┐      ┌──────────────────┐
│   Analyze   │      │   Regeneration   │
│   filtrate  │      │   of Adsorbent   │
└─────────────┘      └──────────────────┘
       │                      │
       │                      ▼
       │             ┌──────────────────────┐
       │             │  Mix adsorbent with 200 ml │
       │             │    acetone for 24 hours    │
       │             └──────────────────────┘
       │                      │
       │                      ▼
       │             ┌──────────────────────┐
       │             │   Filter adsorbent   │
       │             └──────────────────────┘
       │                      │
       │                      ▼
       │             ┌──────────────────────────┐
       │             │  Dry adsorbent in 100 ml/min │
       │             │ nitrogen oven @ 140 C for 1 hr │
       │             └──────────────────────────┘
       │                      │
       │                      ▼
       │             ┌──────────────────────┐
       │             │  Slurry dried carbon │
       │             └──────────────────────┘
       │                      │
       │                      ▼
       │             ┌──────────────────────────┐
       │             │   Add carbon to 820 ml    │
       │             │ centrifuge bottles at 250 mg/l │
       │             └──────────────────────────┘
       │                      │
       │                      ▼
       │             ┌──────────────────────┐
       │             │   Adsorb for 24 hrs  │
       │             └──────────────────────┘
       │                      │
       │                      ▼
       │             ┌──────────────────────┐
       │             │        Filter        │
       │             └──────────────────────┘
       │                      │
       │                      ▼
       │             ┌──────────────────────┐
       └─────────────┤   Analyze filtrate   │
       │             └──────────────────────┘
       ▼
┌──────────────────────┐
│   Compare results    │
│ of filtrate analyses │
└──────────────────────┘
```

Figure 8.   Regeneration of the explosives-loaded carbons

for 1 hr. The next phase of adsorption of the regenerated carbon was evaluated in the 820-ml centrifuge bottles. The acetone-regenerated carbon was slurried with water, and the carbon was pipetted into the centrifuge bottles. Influent CAAP samples were collected, CAAP water was added to the bottles, and the regenerated carbon/CAAP water was tumbled for 24 hr. After the tumble time was complete, the regenerated carbon was filtered from the sample using in-line filters and Teflon tubing and the treated CAAP waters analyzed for RDX, TNB, TNT, and HMX.

Sample Analysis

Samples were analyzed for RDX, TNB, TNT, and HMX according to methods described in SW 846 8330 by the WES ECB. The analytical detection limit was 0.2 $\mu g/\ell$ for RDX, TNB, TNT, and HMX.

Data Interpretation/Isotherm Preparation

Adsorption isotherms were prepared on log-log plots by plotting X/M on the Y-axis, where X is the mass of RDX, TNB, TNT, or HMX adsorbed (micrograms) and M is grams of adsorbent, versus C on the X-axis, where C is the concentration of RDX, TNB, TNT, or HMX in micrograms/liter in solution phase after adsorption. The concentration of RDX, TNB, TNT, or HMX in the adsorbed phase was determined by calculating the difference between explosive present in the method blank before treatment and solution phase concentration after treatment. Linear regression analysis was used to described the relationship between adsorbed and solution phase concentrations. Adsorption capacity (micrograms/liter) for each adsorbent was determined by setting C = initial concentration of the RDX, TNB, TNT, or HMX and solving the regression equation for X/M.

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4   Discussion of Results

Preliminary Tests

The results of the preliminary tests of each adsorbent are presented in Table 9. These data represent the average of the duplicate runs. Individual replicate results are presented in Appendix A. When one replicate was less than the analytical detection limit of 0.2 $\mu g/\ell$, the measured concentration was averaged with a value of 0.2 $\mu g/\ell$. For example, the replicate TNT concentrations for Hydrodarco 4000 in Batch 1 were <0.2 $\mu g/\ell$ and 0.6 $\mu g/\ell$ and were averaged to obtain 0.4 $\mu g/\ell$. Three carbons and one carbonaceous resin had average concentrations below 0.2 $\mu g/\ell$ for RDX, TNB, TNT, and HMX at a dosage of 250 mg/ℓ after 24 hr of treatment: Calgon F-400, American Norit ROW 0.8, Westates CC-601, and Ambersorb 572. The three carbons, Calgon F-400, American Norit ROW 0.8, and Westates CC-601 (formed from bituminous coal, extruded coal, and coconut shell, respectively), were selected for further evaluation in isotherm studies. Based on the results of preliminary tests, product of formation did not show a trend for the optimal adsorbents for treatment because one bituminous coal and one coconut shell carbon were selected for evaluation and one bituminous coal and one coconut shell carbon were not selected. Ambersorb 572 was not selected because its bulk costs are significantly higher (see Table 5).

The results of the preliminary tests show TNT as the indicator compound because TNT was the compound measured in the effluent after adsorption treatment, while other explosives were not detected. Three of the adsorbents, Coconut Shell PAC, Hydrodarco 4000, and Calgon F-200, decreased RDX, TNB, and HMX to <0.2 $\mu g/\ell$, but TNT effluent concentrations were greater than the 0.2-$\mu g/\ell$ detection limit. Coconut Shell PAC, Hydrodarco 4000, and Calgon F-200 were not further tested.

Two dosages of Ambersorb 563 and Ambersorb 572, 125 mg/ℓ and 250 mg/ℓ, were evaluated. The 125-mg/ℓ dosage was tested initially to evaluate whether the efficiency of Ambersorb 563 and Ambersorb 572 for removal of RDX, TNB, TNT, and HMX was greater than the carbons, which were evaluated at a dosage of 250 mg/ℓ. The 125-mg/ℓ dosage did not treat RDX, TNB, TNT, and HMX to below the 0.2-$\mu g/\ell$ detection limit using Ambersorb 563 and only removed RDX to below 0.2 $\mu g/\ell$ using Ambersorb 572.

Table 9
Average Results of Preliminary Tests[1]

Batch No.	Adsorbent	Dosage mg/ℓ	Concentration, µg/ℓ			
			RDX	TNB	TNT	HMX
1	Influent	NA	45.3	108.0	241.3	31.2
	Method Blank	NA	39.6	110.2	242.3	33.2
	Hydrodarco 4000	250	<0.2	<0.2	0.4	<0.2
	Coconut Shell PAC	250	<0.2	<0.2	0.8	<0.2
	Calgon F-400	250	<0.2	<0.2	<0.2	<0.2
	Calgon F-200	250	<0.2	<0.2	0.63	<0.2
2	Influent	NA	27.1	113.2	250.9	32.9
	Method Blank	NA	28.1	109.2	241.2	33.0
	Ambersorb 563	125	8.7	12.6	29.3	10.7
	Ambersorb 572	125	<0.2	1.3	5.7	0.6
	Amberlite XAD-4	3,000	3.6	3.5	2.9	4.3
3	Influent	NA	28.2	111.3	246.0	34.3
	Method Blank	NA	29.0	103.1	236.3	34.7
	American Norit ROW 0.8	250	<0.2	<0.2	<0.2	<0.2
	Westates CC-601	250	<0.2	<0.2	<0.2	<0.2
	Biomin EC-100	3,000	4.3	43.4	81.5	1.0
	Clarion PM-100	3,000	8.9	3.3	7.8	9.3
4	Ambersorb 563	250	2.34	1.69	5.02	3.70
	Ambersorb 572	250	<0.2	<0.2	<0.2	<0.2

[1] When one of two replicate concentrations was below detection limit, the detection limit, 0.2 µg/ℓ, was used to determine the average concentration.

The 250-mg/ℓ dosage was evaluated, and Ambersorb 572 removed RDX, TNB, TNT, and HMX to below 0.2 µg/ℓ. The minimal dosage required for treatment was not determined for Ambersorb 572 because adsorbent costs are approximately 50 times higher for Ambersorb 572 than for carbons. The 250-mg/ℓ dosage of Ambersorb 563 did not treat any of the explosives to below 0.2 µg/ℓ.

Biomin EC-100, Clarion PM-100, and Amberlite XAD-4 were evaluated at a dosage of 3,000 mg/ℓ and did not treat RDX, TNB, TNT, or HMX to less than 0.2 µg/ℓ and were not further tested. Of the organophilic clays, Clarion PM-100 was the most effective, but did not treat the CAAP waters to below the drinking water standard of 2 µg/ℓ for RDX, TNB, or TNT. Neither

Amberlite XAD-4 nor Biomin EC-100 treated RDX, TNB, and TNT to below 2 $\mu g/\ell$, the treatment goal selected for comparison purposes.

Equilibrium Time Results

The average results of equilibrium time determination tests are presented in Table 10. Individual replicate results are presented in Appendix A. The equilibrium time required for adsorption was determined as that time when the concentration of RDX, TNB, TNT, and HMX in the solution phase was the

Table 10						
Average Results of Equilibrium Time Determination Tests						
Batch No.	Adsorbent	Contact Time, hr	Concentration, $\mu g/\ell$			
			RDX	TNB	TNT	HMX
1	Influent	NA	51.63	123.0	256.4	36.90
	Method Blank	24	49.35	113.45	228.25	34.73
	Calgon F-400	0	<0.2	<0.2	0.21	<0.2
		1	<0.2	<0.2	<0.2	<0.2
		2	<0.2	<0.2	<0.2	<0.2
		4	<0.2	<0.2	<0.2	<0.2
		8	<0.2	<0.2	<0.2	<0.2
		24	<0.2	<0.2	<0.2	<0.2
2	Influent	NA	46.19	111.45	232.7	32.25
	Method Blank	NA	43.20	102.38	214.25	30.59
	Westates CC-601	0	<0.2	<0.2	1.05	<0.2
		1	<0.2	<0.2	<0.2	<0.2
		2	<0.2	<0.2	<0.2	<0.2
		4	<0.2	<0.2	1.67	0.39
		8	<0.2	<0.2	<0.2	<0.2
		24	<0.2	<0.2	<0.2	<0.2
3	Influent	NA	43.35	103.1	222.35	29.70
	Method Blank	NA	35.98	87.08	184.35	25.55
	American Norit ROW 0.8	0	0.46	0.59	0.41	0.75
		1	<0.2	<0.2	<0.2	<0.2
		2	<0.2	<0.2	<0.2	<0.2
		4	<0.2	<0.2	0.94	0.25
		8	<0.2	<0.2	<0.2	<0.2
		24	<0.2	<0.2	<0.2	<0.2
4	Adsorbent Blank	24	<0.2	<0.2	<0.2	<0.2

lowest and remained constant as contact time increased. Each equilibrium time determination test was conducted using a dosage of 250-mg/ℓ adsorbent. Based upon the results in Table 10, the required contact time for adsorption of RDX, TNB, TNT, and HMX to be adsorbed onto Calgon F-400 was 1 hr. The required contact time for adsorption of RDX, TNB, TNT, and HMX onto Westates CC-601 and American Norit ROW 0.8 was 8 hr. Concentrations of TNT and HMX increased from <0.2 μg/ℓ to 1.67 μg/ℓ and 0.39 μg/ℓ, respectively, for Westates CC-601 and from <0.2 μg/ℓ to 0.94 and 0.25 μg/ℓ, respectively, for American Norit ROW 0.8. Although there is no definite explanation, one possibility is the error associated with dosing at low levels and the inaccuracies associated with weighing such small amounts into the sample containers. Thus, modified methods of dosing were used in later tests. The contact times determined during the equilibrium time determination phase were used during the isotherm evaluations.

Adsorbent blanks were run during this phase of the study to determine whether the adsorbents contained any of the explosive compounds due to manufacturing or other handling procedures. Adsorbent blanks were tested for 24 hr, the longest contact time, to allow maximum contact for any leaching of explosives from the adsorbents to occur. The results of RDX, TNB, TNT, and HMX analysis were less than 0.2 μg/ℓ. Adsorbent blanks were not evaluated further.

Isotherm Results

The averaged results of isotherm evaluations are presented in Table 11. Individual isotherm results are presented in Appendix A. The average results of the isotherm tests indicate that the 2-μg/ℓ criterion for RDX, TNB, and TNT can be met with a carbon dosage of 50 mg/ℓ using Westates CC-601 and American Norit ROW 0.8 and a dosage of 100 mg/ℓ using Calgon F-400. One significant point in Table 11 is that the 100-mg/ℓ dosage of Calgon F-400 treated RDX, TNB, TNT, and HMX to <0.2 μg/ℓ, but the 250-mg/ℓ dosage did not. Although it is impossible to determine the reason for concentrations of RDX, TNB, TNT, and HMX being higher in the 250-mg/ℓ dosage evaluation of Calgon F-400 than in the 100-mg/ℓ dosage, the concentrations are consistently higher for each explosive, indicating possible laboratory error in dosing the 250-mg/ℓ test. Also, the concentrations of TNT in the 25 and 50 mg/ℓ Calgon F-400 treated effluents were 1.93 and 2.63 μg/ℓ, respectively. The increased concentration of TNT could also be due to difficulties in dosing at such low levels (see Table 7). However, the best available method of dosing the CAAP waters was based on published information.

The adsorption capacity of the adsorbents is listed in increasing order in Table 12 for each explosive. However, it is difficult to assign the order of comprehensive effectiveness at removal of all four explosives since Westates CC-601 was the most effective at removal of RDX, TNB, and HMX, and

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Table 11
Average Results of Isotherm Tests

Batch No.	Adsorbent	Dosage, mg/ℓ	Concentration, μg/ℓ			
			RDX	TNB	TNT	HMX
1	Influent	NA	35.18	107.00	232.24	31.28
	Method Blank	NA	28.40	85.61	186.12	25.00
	Calgon F-400	25	3.19	1.93	2.96	1.34
		50	1.27	1.45	2.63	0.69
		100	<0.2	<0.2	<0.2	<0.2
		250	0.33	0.66	1.31	0.30
2	Influent	NA	36.57	102.55	229.73	28.93
	Method Blank	NA	35.07	97.63	217.41	26.30
	Westates CC-601	25	1.75	1.38	8.81	1.37
		50	0.51	0.52	0.72	0.37
		100	<0.2	<0.2	0.24	<0.2
		250	<0.2	<0.2	<0.2	<0.2
3	Influent	NA	52.35	112	255	41.5
	Method Blank	NA	53.4	110	248	42.8
	American Norit ROW 0.8	25	5.87	4.09	4.76	4.87
		50	1.22	0.67	0.59	0.99
		100	0.29	<0.2	<0.2	0.22
		250	<0.2	<0.2	<0.2	<0.2

Table 12
Results of Adsorption Capacity at an Effluent Concentration of 2 μg/ℓ

Explosive	Adsorbent	Adsorption Capacity, mg/g
RDX	Westates CC-601	2.9
	American Norit ROW 0.8	1.8
	Calgon F-400	1.1
TNB	Westates CC-601	8.0
	American Norit ROW 0.8	4.0
	Calgon F-400	3.4
TNT	American Norit ROW 0.8	10.0
	Westates CC-601	6.1
	Calgon F-400	6.0
HMX	Westates CC-601	2.0
	Calgon F-400	1.8
	American Norit ROW 0.8	1.2

American Norit ROW 0.8 was the most effective adsorbent at removal of TNT, the indicator compound. Both American Norit ROW 0.8 and Westates CC-601 treated RDX, TNB, and TNT to below the 2-μg/ℓ drinking water standard using a 50-mg/ℓ dosage. Based on the available information, the order of effectiveness of the adsorbents from most to least based on the isotherm tests was American Norit ROW 0.8 $\cong$ Westates CC-601 > Calgon F-400.

Figures 9 through 12 represent the graphs of the isotherm results for RDX, TNB, TNT, and HMX, respectively. Adsorption capacity (x/M) was determined by subtracting the mass of RDX, TNB, TNT, or HMX (micrograms) in the treated water from the mass of RDX, TNB, TNT, or HMX (grams), respectively, in the methods blanks and dividing by the mass of adsorbent to obtain an adsorption capacity (x/M) in micrograms/gram. Based upon a criterion of 2 μg/ℓ for RDX, TNB, TNT, and HMX, the adsorption capacity of the three adsorbents is presented in decreasing order in Table 12 below. The results of the confirmation tests are slightly different and will be discussed in the next section.

Confirmation Test Results

The average results of the confirmation tests are presented in Table 13. Figures 13 through 16 represent the graphs of the isotherm results for RDX, TNB, TNT, and HMX, respectively. Calgon F-400 isotherms were not prepared for TNB, TNT, and HMX because only one data point was obtained at the 25-mg/ℓ dosage of Calgon F-400. Based upon the data point obtained for each TNB, TNT, and HMX for Calgon F-400, the adsorption capacities based upon a 25-mg/ℓ dosage were 4.0, 8.4, and 1.2 mg/g, respectively, with an effluent concentration of 0.76 μg/ℓ TNB, 0.57 μg/ℓ TNT, and 0.47 μg/ℓ HMX. Based upon a criterion of 2 μg/ℓ for RDX, TNB, TNT, and HMX, the adsorption capacity of the three adsorbents is presented in decreasing order in Table 14 below. Since only one data point was obtained for Calgon F-400, the adsorption capacities are listed as > values. The results of the confirmation tests vary slightly from the initial isotherm tests and indicate that the order of effectiveness from most to least effective is Calgon F-400 > Westates CC-601 > American Norit ROW 0.8 since a 50-mg/ℓ dosage of Calgon F-400 treated TNB, TNT, and HMX to < 0.2 μg/ℓ and the RDX concentration using a 50-mg/ℓ dosage was 0.35 μg/ℓ. The 2 μg/ℓ RDX, TNB, and TNT criterion was met using Calgon F-400 at a dosage of 25 mg/ℓ and was met using a 50-mg/ℓ dosage for Westates CC-601 and American Norit ROW 0.8. In the previous tests discussed above, a 100-mg/ℓ dosage of Calgon F-400 was required to treat the explosives to below 2 μg/ℓ. The adsorption capacity of Calgon F-400 for TNT was significantly higher in this phase of testing than in the previous isotherm tests at > 8.4 mg TNT/g of Calgon F-400. Bench-scale column studies would be the most effective method of further evaluating the capacity of the carbons for each of the explosives by evaluating the systems dynamically.

Figure 10. Logarithmic form of Freundlich adsorption iso-
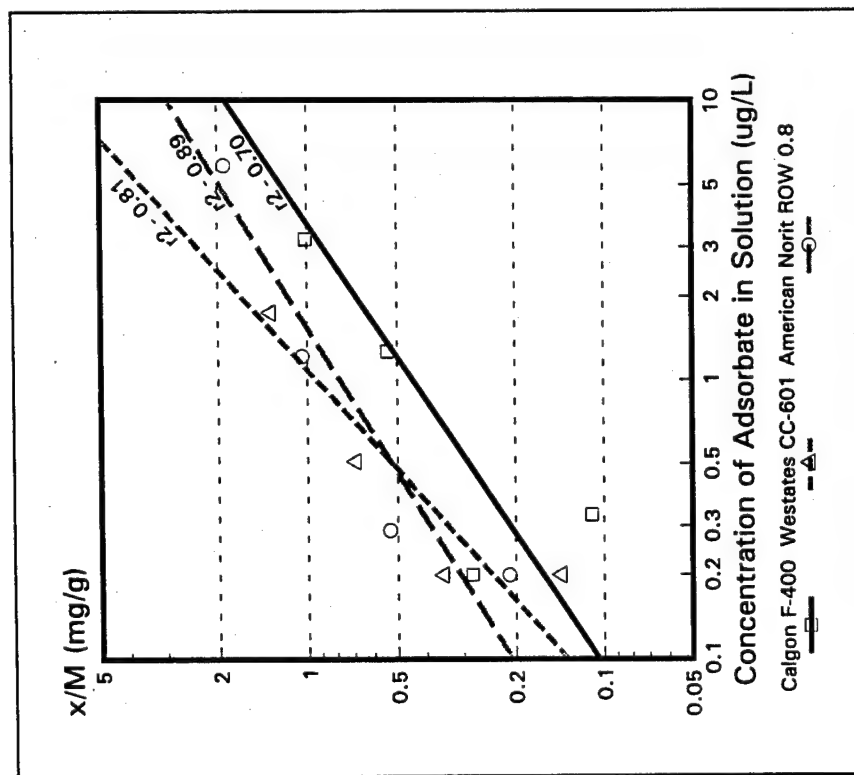therm for TNB on activated carbon

Figure 9. Logarithmic form of Freundlich adsorption iso-
therm for RDX on activated carbon

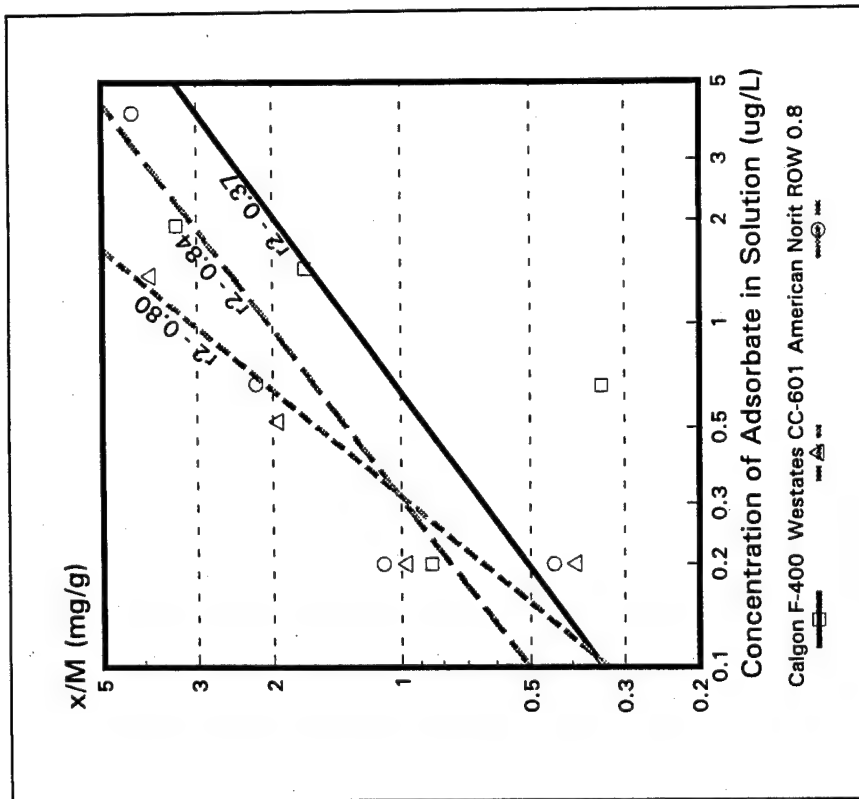Figure 12. Logarithmic form of Freundlich adsorption iso-
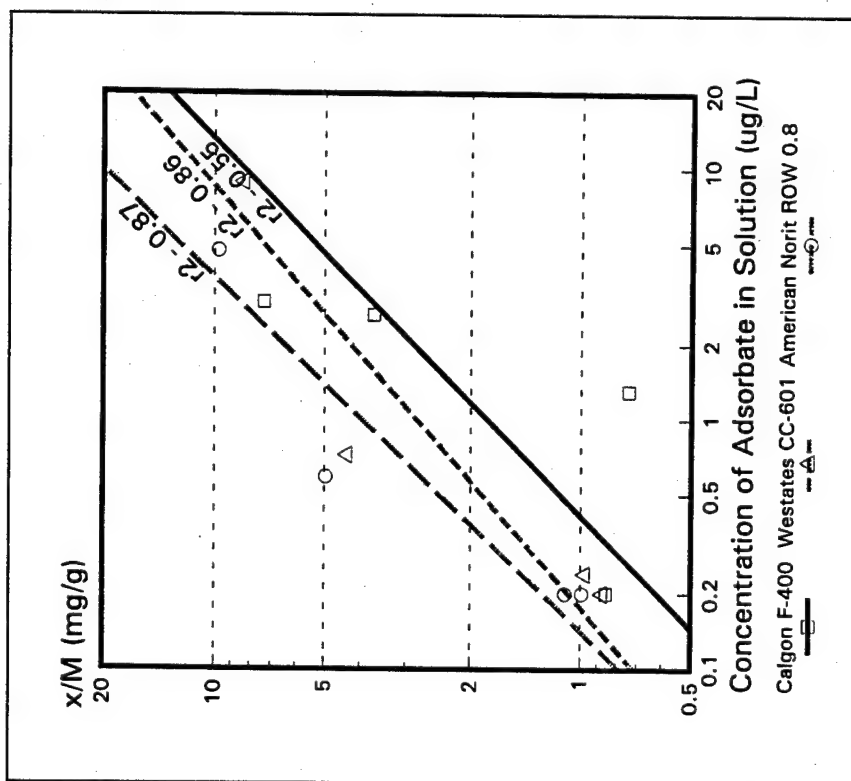therm for HMX on activated carbon

Figure 11. Logarithmic form of Freundlich adsorption iso-
therm for TNT on activated carbon

Table 13
Results of Confirmation Tests

Adsorbent	Dosage, mg/ℓ	Concentration, μg/ℓ			
		RDX	TNB	TNT	HMX
Influent	NA	40.1	104.8	218.5	30.0[1]
Method Blank	NA	39.1	100.6	211.0	29.4[1]
Calgon F-400	25	1.78	0.76	0.57	0.47
	50	0.35	<0.2	<0.2	<0.2
	100	<0.2	<0.2	<0.2	<0.2
	250	<0.2	<0.2	<0.2	<0.2
Westates CC-601	25	2.49	2.21	2.94	1.89
	50	0.62	0.59	0.76	0.43
	100	0.22	<0.2	0.20	<0.2
	250	<0.2	<0.2	<0.2	<0.2
American Norit ROW 0.8	25	8.24	7.58	10.90	6.33
	50	1.73	1.00	0.95	1.23
	100	<0.2	<0.2	<0.2	<0.2
	250	<0.2	<0.2	<0.2	<0.2

[1] Represents an average of two replicates for each explosive.

The results of the screening, isotherm, confirmation, and regeneration tests are presented in Table 15 according to dosage. The results of isotherm evaluations of Calgon F-400 were higher than the results of confirmation evaluations of Calgon F-400 at dosages of 250, 50, and 25 mg/ℓ Calgon F-400. It is beyond the scope of this study to identify the cause of the data discrepancy, but as previously stated, it may be due to problems associated with dosing the CAAP waters at such low levels (see Table 7). Westates CC-601 results were comparable for dosages of 250, 100, and 50 mg/ℓ Westates CC-601. The results of a 25-mg/ℓ Westates CC-601 dosage for the isotherm evaluation were less than the results obtained in the confirmation evaluations with the exception of TNT, which was approximately three times higher in the isotherm evaluations than in the confirmation evaluations. American Norit ROW 0.8 results were comparable for the 250- and 100-mg/ℓ dosage, but the results of the confirmation evaluations were consistently higher for the 25- and 50-mg/ℓ dosages.

Based upon the screening, isotherm, and confirmation evaluations, any of the three carbons evaluated will remove RDX, TNB, TNT, and HMX to below the target levels. In order to determine the optimal adsorbent of the three, pilot-scale column studies are suggested before design of a full-scale system.

Figure 14. Logarithmic form of Freundlich adsorption iso-
therm for TNB on activated carbon (confirmation
tests)
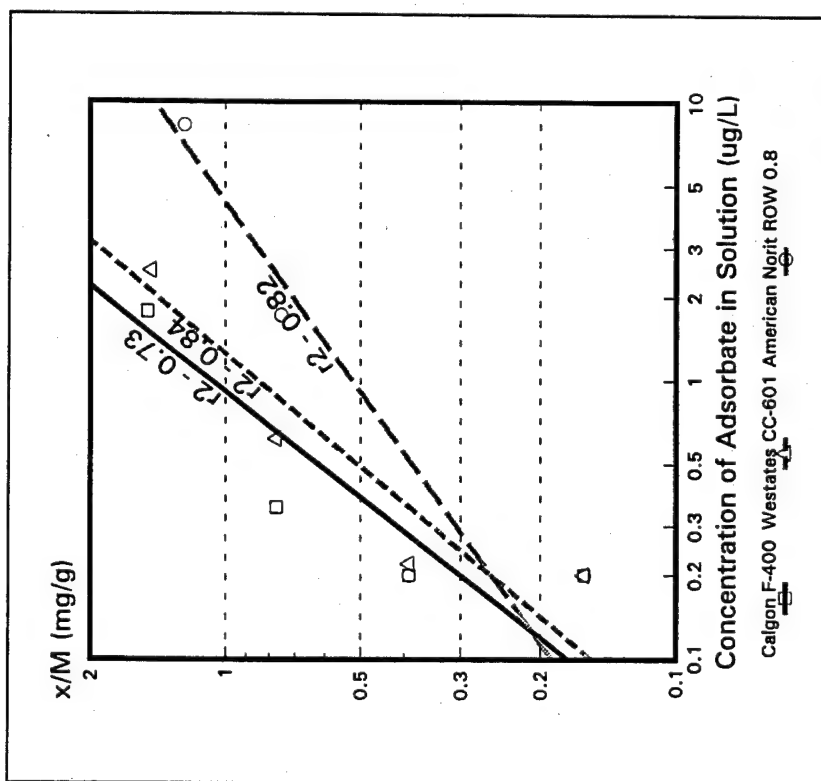
Figure 13. Logarithmic form of Freundlich adsorption iso-
therm for RDX on activated carbon (confirmation
tests)

Figure 16. Logarithmic form of Freundlich adsorption isotherm for HMX on activated carbon (confirmation tests)

Figure 15. Logarithmic form of Freundlich adsorption isotherm for TNT on activated carbon (confirmation tests)

Table 14
Results of Adsorption Capacity at an Effluent Concentration of 2 µg/ℓ (confirmation tests)

Explosive	Adsorbent	Adsorption Capacity, mg/g
RDX	Calgon F-400	2.0
	Westates CC-601	1.5
	American Norit ROW 0.8	0.7
TNB	Calgon F-400	>4.0
	Westates CC-601	4.0
	American Norit ROW 0.8	2.0
TNT	Calgon F-400	>8.4
	Westates CC-601	6.5
	American Norit ROW 0.8	4.5
HMX	Calgon F-400	>1.2
	Westates CC-601	1.2
	American Norit ROW 0.8	0.5

Regeneration Results

The average results of regeneration evaluations are presented in Table 15. The results indicate that regenerated Westates CC-601 can treat RDX, TNB, TNT, and HMX to <0.2 µg/ℓ. Regenerated Calgon F-400 was not as effective and did not remove RDX and TNB to below the criterion of 2 µg/ℓ. The regeneration of American Norit ROW 0.8 was evaluated twice because the results of duplicate testing were not repeatable. One of the replicate runs is presented in Table 15. RDX, TNB, and HMX concentrations were less than the drinking water standard of 2.0 µg/ℓ for RDX and TNB using regenerated American Norit ROW 0.8, but the concentration of TNT was 3.0 µg/ℓ, above the 2.0-µg/ℓ requirement for TNT. Another replicate run was conducted and the results were all <0.2 µg/ℓ for RDX, TNB, TNT, and HMX influent (samples were not recollected).

Table 15
Comparison of Results of Screening, Isotherm, Confirmation, and Regeneration Tests

Test	Adsorbent	Dosage mg/ℓ	Concentration, $\mu g/\ell$			
			RDX	TNB	TNT	HMX
Screening	Calgon F-400	250	<0.2	<0.2	<0.2	<0.2
Isotherm			0.33	0.66	1.31	0.30
Confirmation			<0.2	<0.2	<0.2	<0.2
Regeneration[1]			<0.2	<0.2	<0.2	<0.2
Regenerated[2]			2.3	6.5	<0.2	3.4
Isotherm		100	<0.2	<0.2	<0.2	<0.2
Confirmation			<0.2	<0.2	<0.2	<0.2
Isotherm		50	1.27	1.45	2.63	0.69
Confirmation			<0.2	<0.2	<0.2	<0.2
Isotherm		25	3.19	1.93	2.96	1.34
Confirmation			1.78	0.76	0.57	0.47
Screening	Westates CC-601	250	<0.2	<0.2	<0.2	<0.2
Isotherm			<0.2	<0.2	<0.2	<0.2
Confirmation			<0.2	<0.2	<0.2	<0.2
Regeneration[1]			<0.2	<0.2	<0.2	<0.2
Regenerated[2]			<0.2	<0.2	<0.2	<0.2
Isotherm		100	<0.2	<0.2	0.24	<0.2
Confirmation			0.22	<0.2	0.2	<0.2
Isotherm		50	0.51	0.52	0.72	0.37
Confirmation			0.62	0.59	0.76	0.43
Isotherm		25	1.75	1.38	8.81	1.37
Confirmation			2.49	2.21	2.94	1.89
Screening	American Norit	250	<0.2	<0.2	<0.2	<0.2
Isotherm			<0.2	<0.2	<0.2	<0.2
Confirmation			<0.2	<0.2	<0.2	<0.2
Regeneration[1]			<0.2	<0.2	<0.2	<0.2
Regenerated[2]			<0.2	<0.2	<0.2	<0.2
Isotherm		100	0.29	<0.2	<0.2	0.22
Confirmation			<0.2	<0.2	<0.2	<0.2
Isotherm		50	0.51	0.52	0.72	0.37
Confirmation			1.73	1.00	0.95	1.23
Isotherm		25	5.87	4.09	4.76	4.87
Confirmation			8.24	7.58	10.90	6.33

[1] Virgin carbon.
[2] Regenerated carbon.

Table 16
Average Results of Regeneration Evaluations

Batch No.	Adsorbent	Dosage, mg/ℓ	Concentration, $\mu g/\ell$			
			RDX	TNB	TNT	HMX
1	Influent	250	52.4	122.5	267.0	35.8
	Virgin Calgon WPH	.	<0.2	<0.2	<0.2	<0.2
	Influent		53.7	125.5	272.0	36.8
	Regenerated Calgon WPH	250	2.3	6.5	<0.2	3.4
2	Influent		42.8	103.5	225.5	29.9
	Virgin CC-601	250	<0.2	<0.2	<0.2	<0.2
	Influent		43.1	105.8	235.5	30.2
	Regenerated Westates CC-601	250	<0.2	<0.2	<0.2	<0.2
3	Influent		46.3	112.0	244.5	32.1
	Virgin ROW 0.8	250	<0.2	<0.2	<0.2	<0.2
	Influent		46.4	112.5	246.5	32.1
	Regenerated American Norit ROW 0.8	250	1.1	1.5	3.0	1.0*
	Regenerated American Norit ROW 0.8	250	<0.2	<0.2	<0.2	<0.2**

Note: * Represents one replicate only. The other replicate was repeated, and the results are presented at **.

5 Conclusions

Preliminary Tests

Based upon preliminary evaluation of the six carbons, two carbonaceous resins, one polymeric resin, and two organophilic clays, the following conclusions can be made.

a. The four most effective adsorbents for RDX, TNB, TNT, and HMX removal were Westates CC-601, Calgon F-400, American Norit ROW 0.8, and Ambersorb 572.

b. Westates CC-601, Calgon F-400, American Norit ROW 0.8, and Ambersorb 572 removed RDX, TNB, TNT, and HMX to below the target levels of 2 $\mu g/\ell$ for RDX, TNB, and TNT. The effluent concentrations of RDX, TNB, TNT, and HMX were <0.2 $\mu g/\ell$.

c. XAD-4 did not remove RDX, TNB, TNT, or HMX to below the drinking water standards at a dosage of 3,000 mg/ℓ.

d. The two organophilic clays, Biomin EC-100 and Clarion PM-100, did not remove RDX, TNB, TNT, or HMX to below the target levels at a dosage of 3,000 mg/ℓ.

e. Westates CC-601, Calgon F-400, and American Norit ROW 0.8 were selected for isotherm evaluations. Ambersorb 572 was not evaluated further since it costs approximately 50 times as much as the carbons.

Isotherm Tests

Based upon the results of isotherm tests of Westates CC-601, Calgon F-400, and American Norit ROW 0.8, the following conclusions have been drawn.

a. A dosage of 100 mg/ℓ Calgon F-400 removes RDX, TNB, TNT, and HMX to below the detection limit of 0.2 $\mu g/\ell$.

b. A dosage of 250 mg/ℓ of Westates CC-601 and American Norit ROW 0.8 removed RDX, TNB, TNT, and HMX to below 0.2 μg/ℓ.

c. A dosage of 50 mg/ℓ of Westates CC-601 and American Norit ROW 0.8 removed RDX, TNB, TNT, and HMX to below the target levels for RDX, TNB, and TNT of 2 μg/ℓ. A dosage of 100 mg/ℓ Calgon F-400 removed RDX, TNB, TNT, and HMX to below the target levels for RDX, TNB, and TNT of 2 μg/ℓ.

d. Westates CC-601 had the highest adsorption capacity for RDX, TNB, and HMX of the carbons tested. The capacities were 2.9, 8.0, and 2.0 mg/g for RDX, TNB, and HMX, respectively.

e. American Norit ROW 0.8 had the highest adsorption capacity for TNT of 10.0 mg/g.

Confirmation Tests

The results of the confirmation tests confirmed the following:

a. The confirmation test results verified that RDX, TNB, TNT, and HMX concentrations in the CAAP waters could be treated to the target levels using Calgon F-400, Westates CC-601, and American Norit ROW 0.8.

b. The order of effectiveness of the adsorbents is Calgon F-400 > Westates CC-601 > American Norit ROW 0.8.

c. A dosage of 25 mg Calgon F-400/ℓ of CAAP water treated the CAAP waters to the target levels of 2 μg/ℓ RDX, TNB, TNT, and HMX. The Westates CC-601 and American Norit ROW 0.8 required 50-mg/ℓ dosages to reach the target levels.

d. Calgon F-400 had the highest adsorption capacity for RDX, TNB, TNT, and HMX of the carbons tested. The capacities were 2.0, 10.3, 45.0, and 10.5 mg/g for RDX, TNB, TNT, and HMX, respectively.

Regeneration Tests

The results of the regeneration studies provide the following conclusions:

a. All three carbons, Westates CC-601, Calgon F-400, and American Norit ROW 0.8, can be regenerated using acetone and reused to further treat explosives-contaminated CAAP waters.

b. Regenerated Westates CC-601 removed RDX, TNB, TNT, and HMX
       to below 0.2 $\mu g/\ell$.

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Appendix A
Individual Analytical Results

Table A1
Results of Preliminary Tests

Batch No.	Adsorbent	Dosage mg/ℓ	Replicate	Concentration, $\mu g/\ell$			
				RDX	TNB	TNT	HMX
1	Influent	NA	1	46.0	107.0	234.0	30.7
			2	47.4	110.0	246.0	31.4
			3	42.5	107.0	244.0	31.5
	Method Blank	NA	1	49.9	108.0	244.0	32.5
			2	29.2	112.5	240.6	33.9
	Hydrodarco 4000	250	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	0.6
	Coconut Shell PAC	250	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	1.4
	Calgon WPH	250	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
	Calgon WPL	250	1	<0.2	<0.2	<0.2	0.76
			2	<0.2	<0.2	<0.2	0.5
2	Influent	NA	1	27.2	115.1	255.3	33.5
			2	26.8	111.8	247.2	32.4
			3	27.2	112.7	250.1	33.2
	Method Blank	NA	1	28.1	105.8	233.6	32.2
			2	28.1	112.6	248.8	33.7
	Ambersorb 563	125	1	10.6	12.5	29.3	10.6
			2	6.7	12.6	29.2	10.8
	Ambersorb 572	125	1	<0.2	2.3	5.6	1.0
			2	<0.2	<0.2	5.8	<0.2
	Amberlite XAD-4	3,000	1	3.6	3.4	2.4	4.2
			2	3.6	3.6	3.3	4.4
3	Influent	NA	1	28.7	114.6	253.2	34.6
			2	27.8	103.4	225.4	33.6
			3	28.2	115.8	259.6	34.6
	Method Blank	NA	1	28.8	104.2	241.2	34.9
			2	29.1	101.9	231.3	34.5
	American Norit ROW 0.8	250	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
	Westates CC-601	250	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
	Biomin EC-100	3,000	1	4.4	43.8	82.1	1.1
			2	4.2	42.9	80.8	0.9
	Clarion PM-100	3,000	1	9.1	3.7	8.5	9.5
			2	8.6	2.9	7.1	9.1
4	Ambersorb 563	250	1	2.35	1.56	5.03	3.61
			2	2.32	1.82	5.01	3.78
	Ambersorb 572	250	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2

Table A2
Results of Equilibrium Time Determination Tests

Batch No.	Adsorbent	Contact Time, hr	Replicate	Concentration, $\mu g/\ell$			
				RDX	TNB	TNT	HMX
1	Influent	NA	1	50.54	119.1	250.1	35.89
			2	52.71	126.9	262.7	37.9
	Method Blank	24	1	48.64	110.5	220.2	34.41
			2	50.06	116.4	236.3	35.04
	Calgon WPH	0	1	<0.2	<0.2	<0.2	<0.2
			2	0.2	<0.2	0.21	<0.2
		1	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
		2	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
		4	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
		8	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
		24	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
2	Influent	NA	1	45.51	110.7	229.0	31.94
			2	46.87	112.2	236.4	32.55
	Method Blank	NA	1	45.14	105.6	222.0	31.43
			2	41.25	99.15	206.5	29.74
	Westates CC-601	0	1	<0.2	<0.2	1.68	<0.2
			2	<0.2	<0.2	0.41	<0.2
		1	1	<0.2	<0.2	0.1	<0.2
			2	<0.2	<0.2	<0.2	<0.2
		2	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
		4	1	<0.2	<0.2	3.13	0.57
			2	<0.2	<0.2	<0.2	<0.2
		8	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
		24	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2

(Continued)

Table A2 (Concluded)

Batch No.	Adsorbent	Contact Time, hr	Replicate	Concentration, $\mu g/\ell$			
				RDX	TNB	TNT	HMX
3	Influent	NA	1	42.88	100.6	219.4	28.94
			2	43.82	105.6	225.3	30.46
	Method Blank	NA	1	33.81	82.35	174.8	24.1
			2	38.14	91.8	193.9	27.0
	American Norit ROW 0.8	0	1	0.64	0.8	0.62	1.17
			2	0.27	0.38	<0.2	0.32
		1	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
		2	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
		4	1	<0.2	<0.2	1.68	0.3
			2	<0.2	<0.2	<0.2	<0.2
		8	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
		24	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
4	Adsorbent Blank	24	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2

Table A3
Results of Isotherm Tests

Batch No.	Adsorbent	Dosage mg/ℓ	Replicate	Concentration, μg/ℓ			
				RDX	TNB	TNT	HMX
1	Influent	NA	1	35.1	107.1	233.1	31.3
			2	35.2	106.8	231.4	31.2
	Method Blank	NA	1	30.8	92.5	199.5	27.0
			2	26.0	78.8	172.7	23.0
	Calgon WPH	25	1	3.9	2.3	3.4	1.6
			2	2.5	1.6	2.5	1.1
		50	1	1.7	2.5	4.7	1.1
			2	0.8	0.4	0.6	0.3
		100	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
		250	1	0.5	1.1	2.4	0.4
			2	<0.2	<0.2	<0.2	<0.2
2	Influent	NA	1	35.6	101.2	228.6	28.4
			2	37.5	103.9	230.8	29.4
	Method Blank	NA	1	27.9	81.1	188.2	22.6
			2	42.3	114.2	246.6	30.0
	Westates CC-601	25	1	1.7	1.3	15.8	1.4
			2	1.8	1.5	1.8	1.3
		50	1	0.5	0.5	0.7	0.4
			2	0.5	0.5	0.8	0.4
		100	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	0.2	0.27	<0.2
		250	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2
3	Influent	NA	1	52.6	112.0	255.0	41.9
			2	52.1	112.0	255.0	41.1
	Method Blank	NA	1	54.1	113.0	256.0	39.1
			2	52.7	107.0	239.0	46.4
	American Norit ROW 0.8	25	1	6.4	4.3	5.0	5.2
			2	5.3	3.8	4.5	4.6
		50	1	1.2	0.7	0.6	1.0
			2	1.3	0.7	0.6	1.0
		100	1	0.3	<0.2	<0.2	<0.2
			2	0.3	<0.2	<0.2	<0.2
		250	1	<0.2	<0.2	<0.2	<0.2
			2	<0.2	<0.2	<0.2	<0.2

Table A4
Results of Regeneration Evaluations[1]

Batch No.	Adsorbent	Replicate	Concentration, $\mu g/\ell$			
			RDX	TNB	TNT	HMX
1	Influent	1	54.8	126.0	273.0	36.9
		2	49.9	119.0	261.0	34.7
	Virgin Calgon WPH	1	<0.2	<0.2	<0.2	<0.2
		2	<0.2	<0.2	<0.2	<0.2
	Influent	1	54.4	128.0	276.0	37.6
		2	53.0	123.0	268.0	36.0
	Regenerated Calgon WPH	1	4.4	12.8	<0.2	6.5
		2	<0.2	<0.2	<0.2	<0.2
2	Influent	1	44.7	108.0	237.0	31.2
		2	40.9	99.0	214.0	28.5
	Virgin CC-601	1	<0.2	<0.2	<0.2	<0.2
		2	<0.2	<0.2	<0.2	<0.2
	Influent	1	36.9	94.5	216.0	26.9
		2	49.2	117.0	255.0	33.4
	Regenerated Westates CC-601	1	<0.2	<0.2	<0.2	<0.2
		2	<0.2	<0.2	<0.2	<0.2
3	Influent	1	45.8	111.0	241.0	31.7
		2	46.7	113.0	248.0	32.4
	Virgin ROW 0.8	1	<0.2	<0.2	<0.2	<0.2
		2	<0.2	<0.2	<0.2	<0.2
	Influent	1	47.0	114.0	248.0	32.4
		2	45.8	111.0	245.0	31.7
	Regenerated American Norit ROW 0.8	1	31.7	38.2	71.3	26.5[2]
		2	1.1	1.5	3.0	1.0[3]
	Repeat of Run Above[2]	3	<0.2	<0.2	<0.2	<0.2

[1] Adsorbent dosage is 250 mg/ℓ.
[2] Run was duplicated.
[3] Reported in Table 14.

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13. ABSTRACT (Maximum 200 words)

The Cornhusker Army Ammunition Plant (CAAP) is located in Grand Island, NE, and occupies 11,936 acres (4,832.38 ha) in Hall County. The CAAP is classified as a load, assembly, and pack facility and was constructed in 1942 for the purpose of manufacturing bombs for World War II. Environmental impacts of explosives manufacturing were evaluated in an Installation Assessment Study that identified 58 sources of contamination by explosive compounds. The plant is currently in standby status until completion of environmental studies required for real estate transactions.

The U.S. Army Engineer Waterways Experiment Station (WES) performed evaluations of adsorption and ultraviolet chemical oxidation for remediation of explosives contamination in CAAP waters. Average initial concentrations of 33.5 $\mu g/\ell$ RDX, 110.8 $\mu g/\ell$ TNB, 246.1 $\mu g/\ell$ TNT, and 33.9 $\mu g/\ell$ HMX were analyzed in the samples collected for the WES studies. Adsorption studies included evaluation of carbons, carbonaceous resins, one polymeric resin, and organophilic clays for removal of RDX, TNB, TNT, and HMX. Preliminary tests indicated that RDX, TNB, TNT, and HMX could be reduced to less than 0.2 $\mu g/\ell$ most cost effectively by

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carbons, i.e., Calgon Filtrasorb 400 (F-400), Westates CC-601, and American Norit ROW 0.8. Isotherm evaluations verified results of the preliminary tests and indicated RDX, TNB, TNT, and HMX could be reduced below the current analytical detection limit of 0.2 $\mu g/\ell$. Regeneration tests indicated regenerated Westates CC-601 and regenerated American Norit ROW 0.8 could remove RDX, TNB, TNT, and HMX to less than 0.2 $\mu g/\ell$. Regenerated Calgon F-400 was not as effective as regenerated Westates CC-601 and regenerated American Norit ROW 0.8.